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An International Review of Spectroscopy and
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JULY 1915

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THE ASTROPHYSICAL JOURNAL

AN INTERNATIONAL REVIEW OF SPECTROSCOPY
AND ASTRONOMICAL PHYSICS

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LADY MARGARET LINDSAY HUGGINS

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LADY HUGGINS

By SARAH F. WHITING

Died on March 24, at 8 More's Garden, Chelsea, England, after a long illness, Margaret Lindsay, widow of Sir William Huggins, in her sixty-seventh year.

The achievements of the Victorian age were all passed in review in 1897, the year of Queen Victoria's Diamond Jubilee. In the columns of the London papers was a long list of men whom the Queen delighted to honor, among them but a scant number from the ranks of science, and but one woman even remotely mentioned, and that one Margaret Lindsay Huggins.

Knighthood of the Order of the Bath was conferred upon William Huggins "for the great contributions which, with the collaboration of his gifted wife, he had made to the new science of astro-physics." So it may be said that the wife became Lady Huggins in her own right.

Dr. Huggins was born for research, and under him, as he remarked himself, "the astronomical observatory for the first time had also become a laboratory, and the spectroscope attached to the telescope had shown that the chemistry of the solar system prevailed wherever a star twinkled." For thirteen years Dr. Huggins worked alone, mapping lines of stars by night and of the elements by day.

Meantime, with no aid from the schools, because, as Lady Huggins afterward said, "intellectual justice was denied to women," a collaborer was being prepared. Margaret Lindsay Murray, of Dublin, was as a child a lover of the stars. In her early teens she mapped sun-spots with a little telescope of her own construction. Fascinated by certain unsigned articles on the spectrum in a magazine, she made for herself a little spectroscope, and to her joy saw the dark lines in the solar spectrum. She also took up photography and had attained considerable skill when a happy fate brought to her acquaintance the unknown author of the inspiring articles, and in 1875 she became the wife of Dr. Huggins.

Lady Huggins was possessed of the same characteristics as her husband. Both were full of enthusiasm and yet displayed cool judgment; both were patient, conscientious, exact, resourceful. Henceforth her fine qualities of sight and mind were devoted to furthering her husband's investigations into the chemistry and physics of the heavenly bodies.

An eighteen-inch reflector and fifteen-inch refractor had been purchased by the Royal Society and loaned to the Tulse Hill Observatory. In 1876 the dry-plate process was brought to Dr. Huggins' notice, the telescopes were fitted with photographic plates, and the pair began their pioneer work in photographing the spectra of celestial objects.

The period from 1876 to 1882 was spent in work on the planets to gain experience. Then the eighteen-inch reflector was fitted with two prisms of Iceland spar and Lady Huggins worked with skill guiding the telescope for the long-exposure photographs of the ultra-violet spectra of the stars. She was also most successful in manipulating the plates.

Papers were constantly given out from the Tulse Hill Observatory. Lady Huggins' name appears as joint author of the following: "The Photographic Spectra of Uranus, Saturn, and Mars"; "On the Spectrum, Visible and Photographic, of the Great Nebula in Orion"; "Spectra of Wolf-Rayet Stars in Cygnus"; "Lines in the Photographed Spectrum of Sirius"; "Studies of the Spectrum of Nova Aurigae"; "Laboratory Studies of the Spectra of Calcium and Magnesium under Different Conditions"; "Spectrum of

Radium," etc. Meantime the work for the *Atlas of Representative Stellar Spectra* was kept up until this came out in 1899, with its discussion of the evolution of the stars and its majestic sequence of spectra arranged with the lines of hydrogen and calcium as guides.

To the perfection of detail of this monumental work, both scientifically and aesthetically, Lady Huggins made large contributions.

In 1909 appeared the *Scientific Papers*, under the joint editorship of Sir William and Lady Huggins, and in 1906, also edited by her, *The Royal Society*, a reprint of Sir William's addresses given during the five years of his presidency of the Royal Society, with history and illustrations. The three books just mentioned were in contents and finish such fine specimens of book-making that the life of Sir William upon which she was engaged was justly awaited with anticipation. Her untimely death has interrupted this task, but it is to be hoped that it will be put into the hands of a worthy literary executor.

Many American astronomers can testify that Lady Huggins was not only a scientist but a most gracious and hospitable homemaker. She was mistress of many so-called accomplishments, and possessed much accurate knowledge of art and antiquities, as was witnessed by her brochure on the Astrolabe and articles in the *Encyclopaedia Britannica* and various archaeological journals.

She was, together with her friend Miss Agnes Clerke, whose life she wrote, made an honorary member of the Royal Astronomical Society in 1903. Her genius for friendship was attested by the motto with which she was accustomed to head her letters "Dieu — et mes amis." An intimate friend writes: "Her loss is keenly felt by many and in many ways."

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A THEORY OF ABSORPTION, FLUORESCENCE, AND PHOSPHORESCENCE

By E. C. C. BALY

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INTRODUCTION

During recent years a number of papers have been published describing the absorption spectra of organic compounds, and the

majority of these publications have dealt with the constitution of the compounds, the assumption being made that there exists a definite correlation between the primary structure of a molecule and the type of absorption which it exerts. Perhaps the most striking papers that have been published on this subject are those by Hantzsch, who has established the existence of numbers of series of differently colored salts from colorless acids or bases. To each differently colored salt he attributed a different formula. Now recent investigations in these laboratories into the problem of light-absorption by organic compounds by no means favor the view that there is any direct relation between absorption and constitution, if such relation is held to mean that, when a colored salt is obtained from a colorless acid or base, the parent substance has changed its constitution in the salt. The principal outcome of this work is the establishment of a definite relation, not between primary structure and absorption, but between absorption and chemical reactivity. The evidence obtained is so strong that it is necessary to formulate a new theory to account for the new phenomena, a theory which at the same time must explain all those experimental facts that appear to support the absorption-structure relation.

It is somewhat surprising that in all the work that has appeared dealing with the absorption spectra of organic compounds in relation to their structure no notice has been taken of the absorption exerted by these compounds in the infra-red region of the spectrum. There is at hand a series of most accurate measurements of the absorption of organic compounds in the infra-red, made by Coblenz and others, and it is impossible to doubt that there must exist an intimate relation between the absorption bands as exhibited by a given compound throughout the whole spectrum from extreme ultra-violet to extreme infra-red. In spite of this no attention has been paid to infra-red absorption, and it has been attempted entirely to decide the constitution from arguments based on absorption in the ultra-violet and visible regions alone.

It is proposed in the present paper in the first place to formulate a theory of light-absorption, fluorescence, and phosphorescence, and to show how intimate is the connection between these and chemical reactivity. In the second place it is proposed to apply the energy-

quantum theory to absorption, fluorescence, and phosphorescence throughout the whole spectrum, and to show how it is possible to calculate the wave-lengths of the lines of any absorption-band group in the ultra-violet or visible regions from the wave-lengths of the absorption bands in the infra-red.

PART I. AN ELECTROMAGNETIC FORCE FIELD THEORY OF ABSORPTION

1. *The existence of molecular force fields and a theory of chemical reaction and reactivity.*—It was shown by Humphreys¹ that the phenomena of the Zeeman effect and the pressure-shift of spectrum lines can be explained by the existence of electromagnetic force fields surrounding the atoms. Although so marked a success has attended the application of these fields to the phenomena above noted, their influence upon the properties of molecules has not been considered. It would seem, indeed, that in the existence of molecular force fields we can find the explanation of the phenomena of absorption and fluorescence such as is exerted by compound substances.

Clearly these atomic fields must possess a polar factor as well as a quantity factor, and if the general case be considered of a molecule composed of several atoms of different elements, it is evident that the free and independent existence of the several force fields must represent a metastable condition. A certain amount of condensation must occur between the force lines of the separate fields with the escape of energy and the establishment of a molecular force field. There is little doubt that the properties of any molecule will depend upon its force field. It is not proposed here to enter into a full discussion of how the chemical properties of molecules are determined by their force fields, but it is necessary very briefly to refer to this side of the problem for the proper understanding of what follows.

If two elementary atoms of opposite type are brought together, their respective force fields will condense together with the formation of a molecular field, and within this field there will exist a potential gradient. If this potential gradient be sufficiently steep, one or more electrons will tend to move from one atom to the other,

¹ *Astrophysical Journal*, 23, 233, 1906.

with the result that a true compound of the two elements will be formed. Similarly, when two molecules of different types are brought together, their force fields will tend to condense with the formation of an addition complex. If the potential gradients within this complex be steep enough, there will ensue a rearrangement of electrons and the formation of new chemical individuals. In other words, a chemical reaction will take place, but if the gradients be not sufficiently steep, the addition complex first formed will remain as such. We are therefore enabled to recognize a complete gradation between the condition when a chemical reaction occurs between two molecules and the condition when, owing to their force fields being exactly the same, the molecules have no mutual action whatsoever. This recognition of mutual influence between two molecules when no specific chemical reaction occurs is of great importance both in pure chemistry and in the phenomena of light absorption.

Now when the condensing together of the force lines of the several atomic force fields within a given molecule takes place, it is possible that owing to the relation between the numbers of the force lines the resulting molecular force field may be entirely closed. In such a case the reactivity of the molecule will be nil. On the other hand, there may be left over, after the maximum possible condensation has taken place, an uncompensated balance of force lines. In this case the molecule will possess a definite and measurable reactivity. This last condition is doubtless the explanation of that property known to chemists as residual affinity, while in the former condition is to be found the explanation of the want of reaction between such pairs of compounds as hydrogen chloride and ammonia when all moisture is absent.

According to the present theory, therefore, the reactivity of all atoms and molecules is to be attributed to their electromagnetic fields. Chemical union between atoms, chemical reaction between molecules, are both due to these force fields, and primary valency would seem not to be the *causa causans* of such reactions, but to be a resultant effect. Valency in its stoichiometrical meaning is due to the interatomic rearrangement of the electrons when the potential gradients within the addition complexes at first formed are

sufficiently steep and the electronic transference results in a smaller energy content of the product. The so-called residual affinity is the uncompensated residuum after the maximum possible condensation of the force lines of the molecule has taken place. When this residuum is vanishingly small the molecule exhibits no evidences of chemical reactivity, but when, as is more usually the case, the residuum has a finite value the molecule does possess an observable and measurable reactivity.

2. *The opening up of the closed molecular force fields by the action of a solvent or of light. Theory of selective absorption.*—It is evident from the foregoing that if the closed field of a molecule be opened or unlocked its reactivity will be enhanced. This unlocking may be brought about in one of two ways, namely, by the use of a substance possessing residual affinity or by the action of light. If a compound, the molecules of which possess closed fields, be dissolved in a solvent endowed with residual affinity, the free force lines of the solvent will interpenetrate the closed fields of the solute, with the result that these now will be opened and become capable of reacting with any other suitable substance dissolved in the same solvent. Clearly, however, the case is a perfectly general one. The tendency of molecules possessing residual affinity will always be to open up the closed fields of other molecules when the two molecular types are brought together, whether an actual solution is formed or not. When the two molecular types are brought together a certain proportion of the closed fields will be opened up and an equilibrium will be set up between the opened-up and non-opened-up molecules. Upon this equilibrium the reactivity of the system will depend.

The second method of opening up the closed fields is by the influence of light. Due as they are in the first place to the rotation of the electrons of the constituent atoms, it follows that the force fields must be capable of absorbing those rays of light which have the same frequency as that of the electrons. The light in being absorbed does work upon the closed fields and opens them, and this at once gives a rational explanation of the selective absorption of the light. When a solution of a compound selectively absorbs light the equilibrium previously existent between opened-up and non-opened-up molecules is shifted toward the opened-up or reactive side, a new photodynamic equilibrium being established. In

passing, it may be noted that this affords an explanation of all the phenomena of photocatalysis.

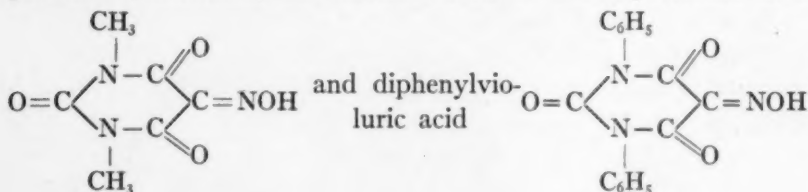
It may perhaps be pointed out that the absorption here referred to, and attributed to the selective absorption of light by the molecular force fields, differs from the fine-line absorption such as is shown by the halogen elements, chlorine, bromine, and iodine, and is no doubt due to the direct action of the electrons themselves. Each of those elements, in addition to their fine-line absorption, also exhibits a broad absorption band in the extreme ultra-violet, and it is this latter which is attributed to the molecular fields. The present theory does not deal with the absorption due to the electrons in their independent action but only with that which is due to the force fields arising from the electronic rotations. That there must be some connection between the two types of absorption seems to be obvious, but at the present time sufficient is not known of both phenomena as exhibited by the same compound to establish the relationship between the two.

3. *The opening up of a complex field must take place in stages, each stage being differentiated by its power of absorbing definite rays of light.*—The mechanism of the opening up of a closed force field may now be dealt with in greater detail. The general statement has been made that a given closed field may be opened up by the influence of a solvent or of light, the action of the light being evidenced by the selective absorption of definite rays. If the case be considered of a complex molecule, it is clear that the force field of that molecule must be complex. There must exist in such a complex field a network of potential gradients, and the influence of a solvent in opening up such a field will depend upon the nature of that solvent. It would be expected that the influence of a solvent on a complex field would be progressive and that it would attack various portions of the field in turn. It indeed follows that the opening up of a complex field must take place in definite stages, the number of such stages depending on the complexity of the field. The free vibration periods of the electrons will depend on the distribution of the force lines within the force field, and as the field is opened up different vibration periods will become active. Hence each stage in the opening up of a given force field will be characterized by its power of absorbing definite light rays and may be

differentiated in this way, since the light rays selectively absorbed by the various stages will be different. The number of possible stages will depend upon the complexity of the field and these stages in turn may be called into play by the use of suitable solvents. Very typical examples of compounds that are opened in stages are the β -naphthalene derivatives which as a rule in alcoholic solution show three absorption-band groups. Three stages in the opening up of the force fields must therefore coexist in this solvent, each one characterized by its power of absorbing definite light rays. In concentrated sulphuric acid solution, on the other hand, the absorption spectra of these compounds are very different, since other stages are called into play, but usually one of these stages at least is common to the two solvents.

Each stage marks a step in the opening up of a given force field and is a function of a given molecule with a definite primary structure. It may be seen at once that this view entirely removes the necessity of postulating a change of primary structure for every variation of absorption evidenced by a given substance with change of solvent. Quite apart from the horrible complexity which is introduced into chemistry by the structure-absorption correlation theory, the view now put forward rests on a scientific basis, which is more than can be claimed for the older notion. Again, in one of his more recent papers Hantzsch¹ is constrained to confess that in at least one case there are not enough different structural formulae to go round, so numerous are the different absorption-curves obtained from one parent substance with different solvents.

Mention was made above of the preparation by Hantzsch² of several differently colored salts from one single colorless acid or base. He found, for example, that the lithium, sodium, potassium, rubidium, and caesium salts of dimethylvioluric acid



¹ *Berichte*, **43**, 1662, 1910.

² Hantzsch and Robison, *Berichte*, **34**, 45, 1910.

vary in color from yellow to blue as the electropositivity of the metal is increased in the salt. The two parent acids are colorless, but owing to their complexity of structure the force fields will be opened in several stages. Manifestly, since the closed field is acid in type, the most suitable substance to open it will be basic in type, and the more basic or electropositive this substance is the higher the stage to which the force field is opened and the longer the wave-length of light that will selectively be absorbed. The series of metals lithium, sodium, potassium, rubidium, and caesium increases in electropositivity with increase in atomic weight, and it follows that the closed field of the parent acid will be opened to increasingly higher stages as the atomic weight of the metal in the salt is increased. The color of the salt will therefore change from yellow through red to blue, since the wave-length of the light selectively absorbed will increase as the higher stages are called into play by the increasing electropositivity of the metal. All the stages in the opening up of a given force field are functions of one primary structure, and thus the present theory readily accounts for the many-hued salts of one colorless acid or base without postulating any change in that primary structure. Similar arguments may be shown to apply to all the results obtained by Hantzsch, but there is no need specifically to deal with these here.

4. *The stages in the opening up of a complex molecular force field proved by the existence of intermediate states in chemical reactions.*—It follows from the preceding general statement of the theory that it is possible to put it to experimental test in a most rigid way. Certain obvious deductions may be drawn which should be capable of clear experimental proof, and it may be said at once that the experimental results afford striking support to the theory.

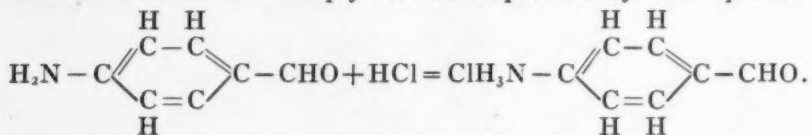
From the chemical point of view the theory established the fact that before any molecule with a closed force field can enter into any reaction it is necessary that its force field be opened up. Again, before a molecule can take part in a specific reaction it is probable that a certain particular stage in the opening of its force fields must be reached. Since such stage will be characterized by its absorptive power, it should be possible to follow the course of the reaction with the spectroscope.

Some years ago Miss Marsden (Mrs. Solomon) and I investigated the absorption spectra of certain aromatic aminoaldehydes and aminoketones.¹ In alcoholic solution each of these compounds exhibits a well-marked absorption band in the ultra-violet. The addition of a trace of an alcoholic solution of hydrogen chloride to any one of these solutions causes the development of a yellow or red color which disappears on the further addition of acid. This color is due to the appearance of a new absorption band at longer wave-lengths than those shown by the parent compounds. On the addition of the excess of acid the absorption changes to that of the hydrochloride of the base, which somewhat resembles the absorption of the free base itself. A typical set of absorption-curves is shown in Fig. 1, and they represent the absorption of

p-aminobenzaldehyde $\text{NH}_2-\text{C} \begin{array}{c} \text{CH}-\text{CH} \\ \text{CH}=\text{CH} \end{array} \text{C}-\text{CHO}$. The full

curve shows the absorption exerted by the aldehyde in alcoholic solution, the dotted curve shows the new absorption band developed in the presence of a trace of alcoholic hydrogen chloride, while the dot-and-dash curve expresses the absorption of the hydrochloride. The curves mark the limits of total absorption at the various concentrations.

It is clear that the conversion of the amino compounds into their hydrochlorides is not simply an addition reaction; that is to say, the reaction is not simply to be expressed by the equation



There is no doubt that it is not the amino compound as it exists in alcoholic solution which forms the salt, but that the first quantity of acid added converts the base into an intermediate form *and that it is this intermediate form which reacts with more acid to form the salt*. These results both extend our knowledge of chemical reaction in that they undoubtedly establish the existence of a hitherto unrecognized intermediate stage, and they also afford strong sup-

¹ *Chemical Society Transactions*, **93**, 2108, 1908.

port to the force-field theory, since it was exactly this phenomenon which was shown above to be foretold by the theory.

The curves given in Fig. 1 make it clear that the entire amino base is not converted into the intermediate and reactive form

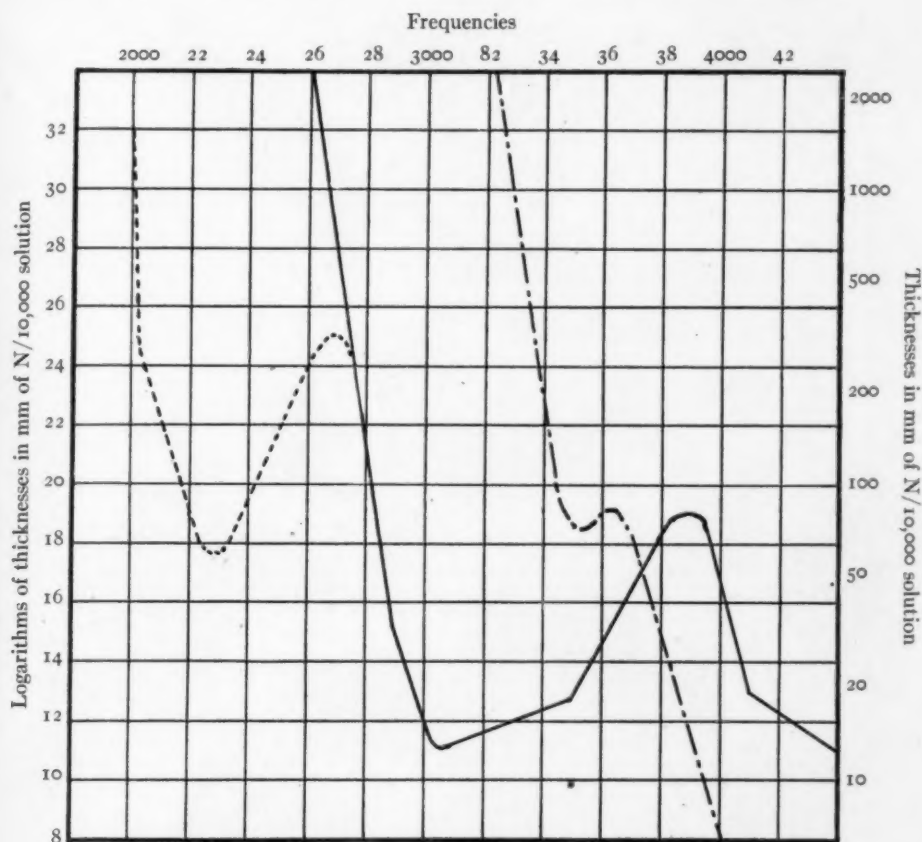
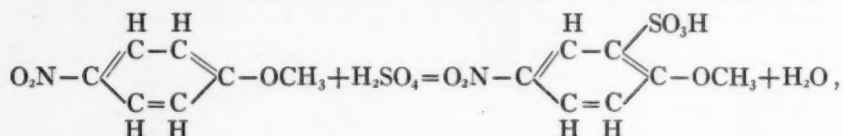


FIG. 1.—*p*-Aminobenzaldehyde

— In alcohol
 - - - - In alcohol + $\frac{1}{10}$ eq. HCl
 - · - · In alcohol + excess of HCl

when the trace of acid is added. This is due to the fact that as the quantity of acid present is slowly increased some of the intermediate stage forms the salt, and at no concentration of acid is it possible to obtain the entire base in the reactive

form without any of the salt being formed. In order to obtain all the reacting molecules in the opened-up or reactive form, it is necessary to deal with some reaction the velocity of which is much slower. Such a reaction was found in the sulphonation of certain aromatic compounds.¹ This reaction in the case of *p*-nitroanisole, for example, is chemically expressed by the equation



but according to the force-field theory the parent substance must pass through an intermediate stage in which its closed force field is opened to some stage higher than that in which it exists in alcoholic solution. If the stage characteristic of the alcoholic solution were sufficiently reactive to give the sulphonic acid, it is obvious that this acid would be formed when an equivalent amount of sulphuric acid is added to that solution. No reaction, however, takes place under those conditions, and in order to form the sulphonic acid it is necessary to dissolve the parent compound in concentrated sulphuric acid, when the sulphonation very slowly takes place. Hence it was to be expected that in solution in concentrated sulphuric acid the force fields would be found to be opened to a higher and more reactive stage. This expectation was fully realized, as may be seen from the absorption-curves shown in Fig. 2, where the full curve is that of the alcoholic solution, the dotted curve that of the strong sulphuric acid solution, and the dot-and-dash curve that of the sulphonic acid obtained by allowing the acid solution to stand for some hours in a warm place. It is perhaps worth mentioning that if the sulphuric acid solution, immediately after preparation, were poured upon ice the parent substance was recovered in a pure state. After the solution had stood a short time the reaction began to take place and its course could be followed throughout with a spectroscope, for the absorption at first shown by the dotted curve in Fig. 2 slowly changed into that shown by the dot-and-dash curve.

¹ Baly and Rice, *Chemical Society Transactions*, **101**, 1475, 1912.

Many compounds were examined in the same way and similar results were obtained in every case. There is thus no doubt that

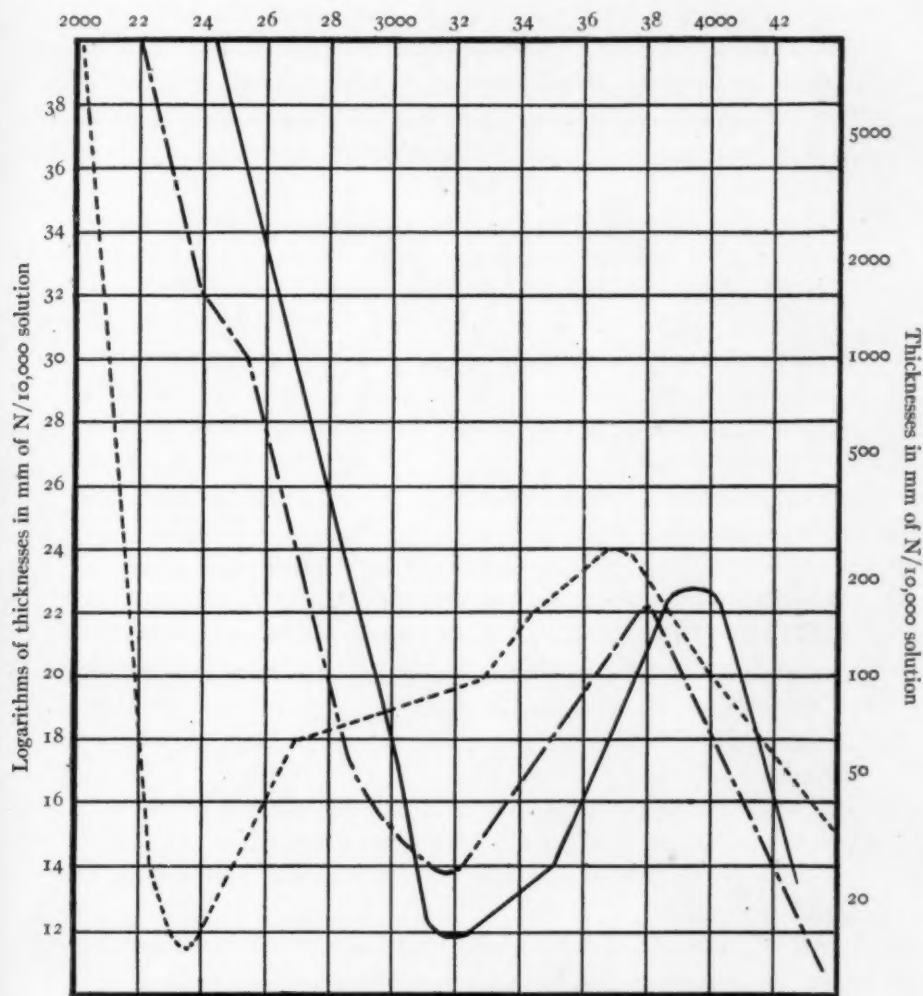


FIG. 2.—*p*-Nitroanisole

- In alcohol
- - - In concentrated sulphuric acid
- · - In concentrated sulphuric acid after standing for some hours

there is established without question the existence of an intermediate stage in a chemical reaction such as was deduced from the force-field theory.

5. *Application of the theory to the explanation of the variation from Beer's law.*—A second method of experimental verification of the theory can be found in the measurement of the absorptive power of a solution and its variation with concentration. As already pointed out, when a compound exists in solution there is an equilibrium set up between the opened-up and non-opened-up molecules of the solute. Such a solution exerts a definite selective absorptive power, a new photodynamic equilibrium being set up. As regards the equilibrium in solution, the position of this may depend on the concentration of the solution. Since any alteration in this equilibrium will undoubtedly entail a change in the absorptive power, we have an explanation of the variation that is so frequently observed from Beer's law. The actual variation to be demanded by the force-field theory is as follows. The ideal case may be considered of a liquid substance and a diactinic solvent, the substance and the solvent must be miscible in all proportions, and, further, on continued dilution of the solution the dark equilibrium must progressively shift toward the reactive side until finally all the solute molecules are opened up. In such an ideal case the molecular absorptive power of the pure liquid will be relatively small since the fields will be more or less closed, so that the light cannot do much work on them. In the presence of a small quantity of the solvent the force fields of a few molecules will be opened up, and, since the light can now do more work on the system, the molecular absorptive power will be increased up to a maximum, i.e., when the light can do the maximum amount of work on the system. Further dilution will then cause a decrease in the absorptive power which, when all the force fields have been opened up, will fall to zero.

It has not as yet been found possible entirely to realize these ideal conditions, which are very nearly realized with ethyl acetoacetate, but two solvents, alcohol and water, are necessary.¹ In Tables I and II are given the absorptive powers of various molecular concentrations of ethyl acetoacetate in alcohol and in water, expressed in terms of the thicknesses of the layers which exert equal absorptive powers. In the first column is shown the

¹ Baly and Rice, *Chemical Society Transactions*, **103**, 91, 1913.

"normality" of the solution, that is to say, the concentration expressed as the number of gram-molecules dissolved in one liter. The first observation, with normality 7.923, refers to the pure liquid ester itself. The second column gives the observed thicknesses which exhibit equal absorptive powers, while the third column shows the calculated thicknesses based on the weaker solutions. As may

TABLE I
ETHYL ACETOACETATE AND ALCOHOL

Normality	Observed Thickness	Calculated Thickness <i>a</i>	Difference Obs. - Calc. <i>b</i>	$\frac{b}{a}$
7.293.....	0.016	0.001893	0.015107	7.4
5.0.....	0.020	0.003	0.017	5.7
2.0.....	0.028	0.0075	0.0205	2.7
1.0.....	0.037	0.015	0.022	1.5
0.5.....	0.05	0.03	0.02	0.67
0.1.....	0.15	0.15	0	0
0.05.....	0.3	0.3	0	0
0.005.....	3.0	3.0	0	0
0.0025.....	6.0	6.0	0	0
0.00125.....	12.0	12.0	0	0
0.001.....	15.0	15.0	0	0
0.0005.....	30.0	30.0	0	0

TABLE II
ETHYL ACETOACETATE AND WATER

Normality	Observed Thickness	Calculated Thickness <i>a</i>	Difference Obs. - Calc. <i>b</i>	$\frac{b}{a}$
0.05.....	6	6	0	0
0.025.....	12	12	0	0
0.01.....	25	30	-5	-0.17
0.002.....	120	150	-30	-0.2
0.001.....	Selective absorption ceased			

be seen in the case of alcohol as the solvent, the molecular absorptive power decreases as the concentration rises and is a minimum with the pure ester. In the case of water as the solvent, the absorptive power begins to decrease with dilution until finally the selective absorption vanishes. The reasons why one single solvent could not be used throughout were twofold. Although alcohol

and the ester are miscible in all proportions, the former is not sufficiently diactinic to allow the use of thicknesses greater than about 30 mm. On the other hand, although water is completely diactinic up to long lengths, it is not miscible in all proportions with the ester.

The results of the observations, however, as far as they go, agree exactly with the deductions from the theory; namely, in passing from a pure substance through gradual decrease in concentration to dilute solution in a diactinic solvent, the absorptive power at first rises to a maximum and then falls to zero. As a more general rule the variation from Beer's law is not exactly of the same type as that shown by ethyl acetoacetate. In most cases the molecular absorptive power increases with dilution up to a maximum after which it remains constant. This type of variation is due to the fact that the equilibrium between opened-up and non-opened-up molecules shifts toward the reactive side with decrease in concentration until it becomes constant, further dilution having no effect. A typical example of this variation is shown by pyridine with water as the solvent (Table III). As can be seen, the molecular

TABLE III
PYRIDINE AND WATER

Normality	Observed Thickness	Calculated Thickness a	Difference Obs. - Calc. δ	$\frac{\delta}{a}$
12.4.....	0.010	0.00064	0.00936	14.7
10.0.....	0.011	0.0008	0.0102	12.7
7.0.....	0.013	0.00114	0.01186	10.4
5.0.....	0.014	0.0016	0.0124	7.7
4.0.....	0.015	0.002	0.0130	6.5
2.0.....	0.019	0.004	0.015	3.7
1.0.....	0.024	0.008	0.016	2.0
0.2.....	0.067	0.04	0.027	0.67
0.02.....	0.000	0.40	0	0
0.002.....	4.0	4.0	0	0
0.0002.....	40.0	40.0	0	0
0.00002.....	400.0	400.0	0	0

absorptive power starts from a minimum with the pure base (12.4 N) and increases until a concentration of 0.02 N is reached, when it becomes constant.

6. *Application of the theory to fluorescence and phosphorescence and the experimental proof.*—The bearing of the force-field theory on fluorescence and phosphorescence may now be considered. It is perhaps not out of place to state the relation that these phenomena bear toward absorption. Speaking generally, no substance can exhibit luminescence unless it is undergoing chemical change or unless it has at some previous time absorbed energy. The first alternative embraces the type of phenomena known as chemiluminescence and refers to those cases where the energy evolution accompanies a chemical change. Although the wave-length of such emitted energy in all probability is characteristic of the substances concerned and therefore is to be explained by the present theory, this cannot be entered into here. The second alternative includes all those cases in which the emission is preceded by an absorption of energy. There are two distinct processes contributing to the phenomenon, namely the absorption and the emission. There is no reason apparent why the velocity of these two should be connected, for the relation between the velocities must depend upon the active substance and the external conditions under which it exists. If the velocity of emission is equal to the velocity of absorption, then the phenomenon will be one of fluorescence, since the emission will not persist after the exciting cause has been removed. If the velocity of emission is slower than that of the absorption, the luminescence manifestly will persist after the exciting cause has been removed, and phosphorescence will be observed. Again, it is possible that owing to the molecular conditions of the active substance the velocity of emission will become vanishingly small. Under these circumstances the absorbed energy will remain stored up in the substance for an indefinite period, or until such time as it is released by special methods. Two such methods are known, one of which is friction and the other is the action of heat. Both are familiar enough and are known as triboluminescence and thermoluminescence respectively. By vigorous friction or by rise of temperature the molecular conditions can be so altered as to cause the velocity of emission to reach a measurable value, with the result that the substance begins to luminesce. The condition in which the substance can exist without any leak of its store of

absorbed energy is a metastable one and the substance returns to its normal condition with the escape of all the absorbing energy when rubbed or heated.

Fluorescence, phosphorescence, triboluminescence, and thermoluminescence may be looked upon as different manifestations of one phenomenon, namely the absorption of energy at one wave-length and the emission at another wave-length. For this reason they are all susceptible of the same explanation, and inasmuch as the force-field theory at once affords a solution of the problem of fluorescence, it may safely be assumed to do the same for the three sister phenomena. As a matter of experimental fact the measurement of the wave-lengths of the emission maxima of fluorescent organic compounds in solution is far more accurate than the measurement of the phosphorescent maxima of solid bodies and therefore it is more satisfactory to deal with fluorescence in the present condition.

Doubts as to the validity of Stokes's law have from time to time been raised by some observers who have indeed categorically stated that under certain circumstances it is possible to obtain fluorescent emission of shorter wave-length than that of the exciting light. Such statements appear to arise from a misconception of Stokes's law and are likely to be misleading. If the absorption-curve of any substance in solution be examined, it will always be found to be very broad, and similarly the emission-curve of fluorescence is also very broad. In very many cases the fluorescent and absorption-curves overlap. The simplest interpretation (which indeed is proved in the second section of this paper) of the breadth of the absorption bands is that all the different wave-lengths lying within the band are connected with one and the same mechanism of absorption. Since the absorption of these wave-lengths gives rise to the fluorescence, it is a fair assumption to make that any one wave-length lying within the absorption band will excite the fluorescence. As the fluorescent band may extend into the region of the absorption band, it will naturally follow that, if the fluorescence is excited by light of a wave-length lying at the extreme red side of the absorption band, some of the fluorescent light will have a shorter wave-length than that of the exciting light. Such over-

lapping cannot be taken as a contradiction of Stokes's law, which surely refers only to the optical centers of the absorption and fluorescence bands.

Numerous measurements have been made of the wave-lengths of the fluorescence maxima of organic compounds with the view of finding the relation between them and those of the absorption bands, but it must be confessed that no great success has attended these investigations. Again, various theories have from time to time been put forward attempting to correlate fluorescence with some type of reversible chemical change. All such theories are open to the most grave objections which, however, need not be entered into here.

As has already been stated, the molecular force-field theory leads to the conclusion that there must exist a number of definite stages in the opening up of any one complex field, each one of which is characterized by its power of absorbing light of definite wave-length. Consequently each stage represents a free vibration-period of the molecular system which, however, is latent as an absorber of light unless a suitable solvent is present. The question now arises, What becomes of the light energy which is absorbed? Manifestly all of it must again be emitted and usually it is assumed to be emitted as heat. It is, however, only reasonable to assume that whatever be the vibration frequency of the emitted energy this frequency must be a characteristic vibration frequency of the absorbing system. When this vibration frequency lies in the infra-red, then of course the energy is emitted as invisible heat radiation. In certain cases, however, some of the energy is emitted in the ultra-violet or visible regions, when we have fluorescence. The vibration frequency of this fluorescent emission must also be characteristic of the molecular system, and, according to the force-field theory, must be characteristic of one of the stages in the opening up of the molecular force field. Fluorescence must therefore be due to the emission of light of a wave-length characteristic of a stage in the opening up of a closed field higher than that stage which is functioning as the absorber. We find on these lines a direct relation between absorption and emission in that they both arise from two stages in the opening up of one given molecular force field.

This explanation of fluorescence may very readily be put to experimental test, for, as already shown, it is possible by the use of suitable solvents to call into play many of the possible stages. It should be possible, therefore, by the use of one solvent to cause a substance to absorb light of the same wave-length as it emits when fluorescing in another solvent. For example, let the case be taken of a substance which in alcoholic solution absorbs light of wave-length λ_1 and fluoresces with emission of light of wave-length λ_2 . It should be possible by the use of another solvent to cause the substance to absorb light of wave-length λ_2 . This relation has been proved to exist in every case that has been examined. Many of the aminoaldehydes and aminoketones dealt with above show fluorescence in alcoholic solution, and the wave-length of the light emitted is the same as that absorbed by these compounds when a trace of alcoholic hydrogen chloride is added to those solutions.¹ Similarly the light absorbed by the aromatic phenol ethers referred to above extends over the same range of wave-lengths as does the fluorescence emission of their alcoholic solution.² Two instances may be quoted, one from each class of compound.

Substance	Fluorescent Band in Solvent 1	Absorption Band in Solvent 2
<i>o</i> -Aminobenzaldehyde	2020-2220	2000-2300
Anisole	2220-3300	2220-3200

These two examples are sufficient to show that the relation holds good and that the force-field theory gives a completely satisfactory explanation of fluorescence.

The bearing of the deviation from Beer's law upon the phenomena of phosphorescence may be noted. Certain facts are now known about phosphorescence;³ namely, that no pure substance will phosphoresce, that phosphorescence is essentially a property of diluted matter, and that there is an optimum of phosphorescence

¹ Baly and Krulla, *Chemical Society Transactions*, **101**, 1469, 1912.

² Baly and Rice, *ibid.*, **101**, 1475, 1912.

³ Lenard and Klatt, *Ann. der Phys.*, **15**, 225, 425, 633, 1904; Urbain and Brunninghaus, *Ann. chim. et phys.*, **18**, 293, 1909.

with a definite concentration of the phosphorogen in the diluent. This is a natural result of such a variation from Beer's law as was described for ethyl acetoacetate in section 5. A pure non-phosphorescing solid exists with its force fields entirely closed, so that they do not selectively absorb the exciting radiation. On mixing the compound with a diluent the force field will be opened so that they can now absorb the exciting energy and hence phosphorescence will ensue. Just as in the case of ethyl acetoacetate the absorptive power and hence the phosphorescent efficiency on increasing dilution reach a maximum and then fall off. The phenomena are therefore exactly those that the theory leads us to expect.

In the present paper the application of the force-field theory to absorption and fluorescence only has been considered, very brief reference being made to the chemical side. It may perhaps be pointed out that the theory can be applied to the phenomena of chemical reaction and reactivity with considerable success. Allotropy and isomerism on the one hand, catalysis and the mechanism of chemical reaction on the other, all seem readily to be explained by the theory, and an account of this will be found in other papers. Reference is made to this side of the general theory in order to emphasize the very intimate connection which is established between chemical properties and the phenomena of selective absorption of light and fluorescence.

PART II. ABSORPTION, FLUORESCENCE, AND PHOSPHORESCENCE IN RELATION TO THE ENERGY-QUANTUM THEORY

1. *The existence of constant differences between the central frequencies of absorption bands, which equal the frequency of an absorption band in the infra-red.*—In the preceding section reference was made to the mechanism by means of which the light energy, previously absorbed by a substance, escapes. There is little doubt that in general the energy is emitted as infra-red radiation, but in certain cases some of the energy is emitted in the ultra-violet or visible regions when we have fluorescence or phosphorescence. Whatever may be the frequency of the emitted energy, there can be no doubt that this frequency must be a characteristic vibration

frequency of the absorbing system. Very little attention seems to have been paid to the destiny of the absorbed energy, the somewhat vague idea apparently being held that it escapes as black-body radiation. Such a notion does not seem to be tenable and would lack a scientific basis, for surely radiation cannot in any case occur except at those frequencies which are characteristic of the absorbing systems. Again it must also be accepted, unless a definite chemical change in state is induced by the absorbed energy—that is to say, unless new stable substances are formed with different energy contents—that the entire absorbed energy must be emitted again at one or more of the characteristic frequencies of the absorbing system.

According to the energy-quantum theory, energy is absorbed and emitted in definite quanta, determined by the product $h\nu$, where h is the Planck constant and ν is the oscillation frequency of the absorbed or emitted radiation. This is the old form of the theory, but recent work by Eucken and others entirely justifies the conclusion that both the emission and the absorption of energy take place in quanta. It follows, therefore, that for every quantum of energy absorbed at one frequency there must be emitted a whole number of quanta at a lower frequency. If ν be the oscillation frequency of the absorbed energy, and ν_x the frequency of the emitted energy in the infra-red, then we have

$$h\nu = xh\nu_x, \text{ and } \nu = x\nu_x,$$

where x is some whole number. Clearly, therefore, the oscillation frequency of the absorbed energy must be a whole multiple of the oscillation frequency of the emitted energy.

Now many substances exhibit several absorption-band groups, as already shown in the first part of this paper, each band corresponding to a stage in the opening up of the force field of the molecular system. The same relation must hold good for each of the absorption bands, and hence if ν_1, ν_2, ν_3 , etc., be the oscillation frequencies of the centers of the absorption bands, we have

$$\nu_1 = \nu_x, \quad x\nu_2 = y\nu_x, \quad \nu_3 = z\nu_x, \text{ etc.,}$$

where x, y, z , etc., are whole numbers. The oscillation frequencies of each absorption band shown by one substance must therefore

be some multiple of the frequency of the infra-red band, and the simplest case will be when the absorption-band frequencies are consecutive multiples of that of the infra-red band.

Again, it has already been shown that a fluorescence or phosphorescence maximum arises from a characteristic vibration frequency of the molecular system. The oscillation frequencies of fluorescence and phosphorescence bands must therefore also be multiples of the frequency of an infra-red band. The final conclusion may be drawn that there must exist a constant difference between the central frequencies of the absorption and fluorescent bands of any one substance and that this constant difference must equal a vibration frequency in the infra-red which is characteristic of that substance. Since the simplest method of determining the characteristic vibration frequencies is by mapping the absorption spectrum, so we may say that the constant difference between consecutive absorption, fluorescent, and phosphorescent bands in the ultra-violet or visible regions must equal the frequency of an absorption band in the infra-red.

In actual practice the relationship may not be quite so simple because consecutive multiples of the infra-red frequency may not always appear, as one or more of these may be latent. This of course does not in any way militate against the soundness of the argument. A very large number of compounds have been investigated in these laboratories and it may be stated that in every case examined, where more than two characteristic vibration frequencies are exhibited whether by absorption or fluorescence, the constant frequency relation holds good. The most striking examples are the β -naphthalene derivatives, which show as a rule three absorption bands and also fluorescent maxima. In these compounds the constant frequencies are extraordinarily accurate when the optical centers of the bands are measured. Unfortunately, however, no measurements have been made of the infra-red absorption of these compounds and therefore the complete relation cannot be verified.

There are, however, one or two compounds which exhibit several absorption bands and fluorescent maxima and for which the frequency of an infra-red band is known. Two may be selected from a

series still under investigation, namely phenol and *m*-cresol. In dealing with the frequencies it is very much simpler to use the reciprocals of the wave-lengths in place of the true oscillation frequencies, and in the following pages the values of $\frac{1}{\lambda}$ are given to four significant figures. Phenol and *m*-cresol both show one absorption band and one fluorescence maximum in neutral alcoholic solution, and in alkaline solution they show two absorption bands and one fluorescent maximum. As none of the frequencies are the same there are five characteristic frequencies in each case. The values of $\frac{1}{\lambda}$ for phenol are as follows:

Neutral solution.....	Fluorescence	3200
	Absorption	3670
Alkaline solution.....	Fluorescence	2890
	Absorption	3370
	Absorption	4170

The extreme difference between the fluorescence maximum and the second absorption band of the alkaline solution is $4170 - 2890 = 1280 = 8 \times 160$. On this basis the maxima can be arranged as in Table IV, the constant frequency difference being taken as 160.

TABLE IV
PHENOL

Calc. $\frac{1}{\lambda}$	Obs. $\frac{1}{\lambda}$		Error
2890.....	2890	Fluorescence in alkaline solution	0
3050.....			
3210.....	3200	Fluorescence in neutral solution	+10
3370.....	3370	Absorption in alkaline solution	0
3530.....			
3690.....	3670	Absorption in neutral solution	+20
3850.....			
4010.....			
4170.....	4170	Absorption in alkaline solution	0

Four of the possible frequencies are latent in the solvents used, but will very probably be observed when other solvents are employed.

Now according to the theory there should be an absorption band in the infra-red with a frequency of 160. Coblenz¹ has measured the infra-red absorption of phenol and finds a very strong band at $\lambda = 6.25 \mu$, the reciprocal of which is 160.

The values of $\frac{I}{\lambda}$ obtained with *m*-cresol are as follows:

Neutral solution	Fluorescence	3100
	Absorption	3610
Alkaline solution	Fluorescence	2920
	Absorption	3440
	Absorption	4120

On the basis of a constant difference of 170 Table V may be given.

TABLE V
m-CRESOL

Calc. $\frac{I}{\lambda}$	Obs. $\frac{I}{\lambda}$		Error
2930	2920	Fluorescence in alkaline solution	+10
3100	3100	Fluorescence in neutral solution	0
3270			
3440	3440	Absorption in alkaline solution	0
3610	3610	Absorption in neutral solution	0
3780			
3950			
4120	4120	Absorption in alkaline solution	0

In the infra-red region there should be an absorption band with a wave-number of 170. Not being able to find any published measurements of the infra-red absorption of *m*-cresol, I have investigated the region about 3μ with a rock-salt prism and a Hilger thermopile. There is a strong band at 2.94μ the frequency of which is 340, and this band is clearly the first multiple of the frequency of a band which must exist at 5.88μ with the frequency of 170. There is no doubt from these results that the relation foretold by the theory is amply confirmed.

In order to guard against misconception it may be pointed out that when a substance fluoresces, the absorbed energy must be emitted both as fluorescent light and as infra-red radiation. If

¹ Publications of the Carnegie Institution of Washington, No. 35, 1905.

ν_1, ν_2, ν_x are the frequencies of absorption, fluorescence, and infra-red radiation respectively, then the relation must hold that

$$h\nu_1 = xh\nu_2 + yh\nu_x,$$

where x and y are whole numbers.

There is another direction in which the present conception can be put to experimental test. It has been shown by Sellmeyer that the refractivities of substances can be connected with an absorption band in the ultra-violet, the relation in its simplest form being given by

$$\mu - 1 = \frac{N}{\nu_0^2 - \nu^2},$$

where N is a constant, ν_0 the oscillation frequency of the ultra-violet band, and ν the oscillation frequency of the light for which a given value of the refractivity, $\mu - 1$, is found. The value of ν_0 is generally very large and lies beyond the working limit of a spectrograph in air and therefore the value has to be calculated from the refractivities for two different values of ν . Recently Mr. and Mrs. Cuthbertson¹ have published the refractivities of several gases for which the wave-lengths of the infra-red absorption bands are known. It should be possible to express these refractivities very accurately by a Sellmeyer formula in which ν_0 is replaced by $x\nu_x$, ν_x being the oscillation frequency of an infra-red band and x some whole number. I have found this to be the case with every gas examined by Mr. and Mrs. Cuthbertson, and the accuracy is shown by the two following instances. In these calculations the true oscillation frequencies have been used.

HYDROGEN CHLORIDE

λ (the mean of the two infra-red bands) = 3.474μ ,² whence $\nu_x = 8.636 \times 10^{13}$. The value of x was found to be 38 and the following formula was used:

$$\mu - 1 = \frac{4.6896 \times 10^{27}}{10769 \times 10^{27} - \nu^2},$$

where $10769 \times 10^{27} = (38\nu_x)^2$.

¹ *Phil. Trans.*, 213 A, 1, 1913.

² Eva von Bahr, *Deutsch. phys. Gesell. Verh.*, 15, 1150, 1913.

TABLE VI
VALUES OF $(\mu-1)10^8$

λ	Calc.	Obs.	Differences
6708.....	44372	44375	-3
6433.....	44444	44444	0
5790.....	44656	44656	0
5770.....	44669	44666	+3
5461.....	44803	44800	+3
5209.....	44930	44930	0
5086.....	45001	45007	-6
4800.....	45187	45187	0

NITRIC OXIDE

λ (mean of the two infra-red bands) = 5.33μ ,¹ whence $\nu_x = 0.56285 \times 10^{14}$. The value of x was found to be 62 and the following formula was used:

$$\mu - 1 = \frac{3.5621 \times 10^{27}}{12233.8 \times 10^{27} - \nu^2},$$

where $12233.8 \times 10^{27} = (62\nu_x)^2$.

TABLE VII
VALUES OF $(\mu-1)10^8$

λ	Calc.	Obs.	Differences
6708.....	29302	29306	-4
6438.....	29346	29334	+2
5790.....	29470	29468	+2
5770.....	29474	29474	0
5461.....	29550	29550	0
5209.....	29626	29622	+4
5086.....	29667	29666	+1
4800.....	29774	29776	-2

The agreement between the calculated and the observed values is exceedingly close and again supports the present theory very strongly. The agreement is certainly as good as Mr. and Mrs. Cuthbertson obtained with Sellmeyer's formula, the constants of which they calculated from the observed refractivities by the method of least squares. The oscillation frequencies thus found for the ultra-violet absorption bands are consequently only theo-

¹ Warburg and Leithauser, *Ann. der Phys.*, **28**, 313, 1909.

retical since they have not been observed and measured. The values given in Tables VI and VII have a materially important advantage in that they have been calculated from an absorption band that has directly been measured and is known, therefore, to be a characteristic function of the substance dealt with.

Before passing on to a further extension of the theory, a possible deduction therefrom may be mentioned. There seems no doubt that absorption, fluorescence, and phosphorescence are directly connected with emission in the infra-red, and hence it would be expected that the converse would be true. In this may be found the explanation of the well-known fact that the phosphorescence of a substance after exposure to an exciting cause is at once destroyed on exposure to infra-red radiation.

2. *Application of the Bjerrum principle to absorption-band groups in the ultra-violet and visible regions. Experimental proof of its validity with absorption, fluorescent, and phosphorescent bands.*—Throughout the preceding portion of this paper no attention has been paid to the breadth of the absorption and fluorescent bands. All the relationships have been based on the frequencies of the optical centers of the bands, whether these latter be in the ultra-violet, visible, or infra-red regions of the spectrum. It is now proposed to discuss the breadth of the bands, and inasmuch as any single band is in reality composed of a group of fine absorption lines it is obvious that the relations described above cannot be considered to be complete unless the whole structure of any given band group can be explained by means of it. This explanation is to be found in a theory put forward by Bjerrum,¹ which when superposed on the theory advanced in this paper appears to give a complete solution of the whole problem. Bjerrum dealt with the absorption bands in the short-wave infra-red region and pointed out that if ν_x be the frequency characteristic of the atoms in a given molecule, then, if ν_r be the frequency of rotation of the molecules, three absorption bands will be shown close to ν_x . The frequencies of these bands will be $\nu_x + \nu_r$, ν_x , and $\nu_x - \nu_r$, respectively, and since the central vibration is pure it will evidence itself only as a very narrow absorption line and will probably escape detection owing to the

¹ *Nernst Festschrift*, p. 90, 1912.

comparatively large slit-width necessary in infra-red work. The result will be that the whole absorption band will appear to be double, each portion being broad, since ν_r represents the average rotational frequency of the molecules.

Bjerrum further pointed out, however, that on the energy-quantum theory, the rotational frequencies must be discontinuous and that they must have well-defined values given by the formula

$$\nu_r = \frac{nh}{2\pi^2 I},$$

where h is the Planck constant, I the moment of inertia, and $n=1, 2, 3, \dots$ etc. As a result of this an absorption-band group in the short-wave region of the infra-red should consist of a series of maxima symmetrically distributed about a central line of frequency ν_x . Each pair of maxima will correspond to a definite rotational frequency of the molecules and hence to an absorption band in the long-wave region of the infra-red. Fraulein von Bahr,¹ has made very accurate measurements of the absorption band shown by water-vapor at $\lambda=6.25 \mu$ and found clear evidence of these pairs of maxima. From these she calculated the wave-lengths corresponding to the rotational frequencies and showed an excellent agreement with the measurements of the absorption bands of water-vapor in the long-wave infra-red region by Rubens and von Wartenberg. Eucken² pointed out that a still closer agreement is obtained on the basis of there being two degrees of freedom possessed by the water molecule, that is to say, two values of I in Bjerrum's formula. The experimental evidence therefore most strongly supports Bjerrum's theory.

There seems to be no valid reason why Bjerrum's conception should not be extended and applied to the absorption-band groups in the visible and ultra-violet regions. If ν be a characteristic vibration frequency, for example, in the ultra-violet, then we should find pairs of absorption lines in the band group with frequencies equal to $\nu + \nu_x$, where ν_x stands for the frequencies of the centers of the short-wave infra-red bands. Some preliminary support

¹ *Phil. Mag.*, **28**, 71, 1914.

² *Deutsch. phys. Gesell. Verh.*, **15**, 1159, 1913.

for this extension of Bjerrum's theory is gained from the fact that the ultra-violet absorption-band group of benzene consists of about 200 fine absorption lines and these form nine well-marked sub-groups which obviously are arranged symmetrically around a central position. This also is the case with several other compounds.

Again, it follows from the theory developed in this paper that the same structure should be found in the case of the fluorescent and phosphorescent bands of the same substance. I have calculated the values of the absorption lines of one or two compounds and find that they form in each case a series of pairs symmetrically distributed about a central line and that the frequency of each short-wave infra-red band has a corresponding line or pair of lines forming part of the structure of the ultra-violet absorption-band group. In short, the application of the Bjerrum conception is completely successful. The compounds may be considered in detail.

BENZENE

Hartley¹ stated that the ultra-violet absorption-band group of benzene can be divided into ten sub-groups, the values of $\frac{1}{\lambda}$ being 3745, 3802, 3861, 3963, 4055, 4148, 4237, 4299, and 4388, respectively. These may be arranged around the one at $\frac{1}{\lambda} = 4055$ as center, as shown in Table VIII. In the third column of

TABLE VIII

λ IN ANGSTROMS	$\frac{1}{\lambda}$	ν_x	MEAN ν_x	INFRA-RED BANDS	
				Calc.	Obs.
2670.....	3745	310	3.23 μ	3.25 μ
2630.....	3802	253	249	4.08
2590.....	3861	194	5.15
2523.....	3936	92	92.5	10.81	10.78
2466.....	4055	0
2411.....	4148	93	92.5	10.81	10.78
2360.....	4237	182	5.50	5.41
2335.....	4282	227	4.40	4.40
2326.....	4299	244	249	4.08
2279.....	4388	333	3.00

¹ *Phil. Trans.*, 208 A, 475, 1908.

the table are given the frequency differences between each line and the central line, and in the fourth column the means between the two values where such exist. The values of $\frac{1}{\nu_x}$ or the wave-lengths of the infra-red bands are given in the fifth column, while in the last column are to be found the wave-lengths of the absorption bands as measured by Coblenz.¹ Four of the calculated bands were observed by Coblenz and the agreement is exceedingly good.

On the other hand, there are 16 absorption bands shown by benzene between $3\ \mu$ and $15\ \mu$, which latter is the upper limit reached by Coblenz, and the question arises whether each of these gives rise to a corresponding pair of lines in the ultra-violet band group when compounded with the central vibration 4055. The complete list is given in Table IX, and, as can be seen, every infra-red band gives an absorption line or pair of lines in the ultra-violet. Certain of the calculated infra-red bands have not been observed by Coblenz and they are included in the table because the corresponding ultra-violet lines were given by Hartley as the heads of the sub-groups. Hence the presumption would be in favor of their being important lines. It will be seen in the sequel, however, that Hartley was apparently incorrect in his measurements of the heads of the sub-groups.

From what has gone before it is clear that the frequency of the central line, 4055, must be a whole multiple of the frequency of one of the infra-red bands. This number is almost exactly 10×405 , which corresponds to a wave-length of $2.47\ \mu$, a value exceedingly close to that measured by Coblenz, namely $2.49\ \mu$. Now the next smaller multiple of 405 is $9 \times 405 = 3645$, and this should form the central line of the fluorescence bands of benzene. The fluorescence of an alcoholic solution of benzene has accurately been measured by Dickson,² who found six bands with frequencies $\left(\frac{1}{\lambda}\right)$ of 3436, 3537, 3631, 3733, 3795, and 3848, respectively. In order that these may be compared with the absorption measurements

¹ *Loc. cit.*

² *Zeit. wiss. Phot.*, 10, 166, 1912.

(which were made with benzene vapor) they must be corrected for the effect of the solvent, which tends to shift the maxima toward the red. Hartley found that this correction is of the order of 15

TABLE IX
BENZENE ABSORPTION (HARTLEY)

λ IN ANGSTROMS	$\frac{1}{\lambda}$	ν_x	MEAN ν_x	INFRA-RED BANDS	
				Calc.	Obs.
2687.....	3722	333	333	3.00 μ
2670.....	3745	310	3.23	3.25 μ
2630.....	3802	253	249	4.08
2612.....	3828	227	228	4.38	4.40
2600.....	3847	208	208	4.80	4.90
2591.....	3861	194	194	5.15
2581.....	3873	182	182	5.50	5.41
2567.....	3895	160	160	6.23	6.20
2560.....	3907	148	148	6.75	6.75
2552.....	3917	138	138	7.25	7.25
2546.....	3928	127	127	7.85	7.80
2538.....	3940	115	115	8.67	8.67
2529.....	3954	101	101.5	9.85	9.78
2526.....	3958	97	97	10.30	10.30
2523.....	3963	92	92.5	10.81	10.78
2519.....	3970	85	85	11.80	11.80
2516.....	3974	81	81	12.30	12.45
2514.....	3978	77	77	12.95	12.95
2466.....	4055	0
2420.....	4132	77	77	12.95	12.95
2418.....	4136	81	81	12.30	12.45
2416.....	4140	85	85	11.80	11.80
2411.....	4148	93	92.5	10.81	10.78
2409.....	4152	97	97	10.30	10.30
2406.....	4157	102	101.5	9.85	9.78
2398.....	4170	115	115	8.67	8.67
2391.....	4182	127	127	7.85	7.80
2386.....	4193	138	138	7.25	7.25
2379.....	4203	148	148	6.75	6.75
2372.....	4215	160	160	6.23	6.20
2360.....	4237	182	182	5.50	5.41
2354.....	4249	194	194	5.15
2346.....	4263	208	208	4.80	4.90
2334.....	4284	229	228	4.38	4.40
2326.....	4299	244	249	4.08
2279.....	4388	333	333	3.00

units, and if 14 be added to the third of the foregoing frequencies we have 3645, which, as already shown, should be the central line of the fluorescence system. It may be assumed that 14 must be added to all Dickson's values, and this is done in the third column

of Table X. In the fourth column are given the frequency differences from the central line 3645, and in parentheses are given the mean values for the corresponding intervals in the absorption-band group as shown in Table IX.

TABLE X
BENZENE FLUORESCENCE (DICKSON)

λ in Angstroms	$\frac{I}{\lambda}$	$\frac{I}{\lambda} + 14$	ν_x
2910.....	3436	3450	195 (194)
2827.....	3537	3551	94 (92.5)
2754.....	3631	3645	0
2679.....	3733	3747	102 (101.5)
2635.....	3795	3809	164 (160)
2599.....	3848	3862	217 (208)

When the substitution products of benzene are considered, some difficulty tends to arise owing to the fact that the molecule becomes unsymmetrical. There is no doubt that the regularity of the structure of the ultra-violet absorption-band group of benzene is due to the symmetry of the molecule; in toluene and its homologues much of this symmetry disappears and hence it cannot be expected that the absorption should be so symmetrical. While *p*-xylene shows considerable symmetry, as already pointed out by Miss Marsden and myself,¹ toluene, *o*-xylene, and *m*-xylene evidence want of symmetry by the fact that there are fewer separate absorption lines on the ultra-violet side of the central line.

TOLUENE

The ultra-violet absorption-band group of toluene has been measured by Hartley,² Grebe,³ and Cremer.⁴ Grebe was the first to arrange the absorption lines in series with constant frequency differences, and although Hartley considered that such arrangement was unjustified, Cremer also arranged the lines in several such series. There would seem to be no doubt that Cremer's values

¹ *Chemical Society Transactions*, **87**, 1347, 1905.

² *Loc. cit.*

³ *Zeit. wiss. Phot.*, **3**, 376, 1905.

⁴ *Ibid.*, **10**, 349, 1912.

are the most accurate, and they are used in Table XI in which they are arranged around the line $\frac{1}{\lambda} = 4047$ as center. The general arrangement of the table is the same as that of Table IX. There

TABLE XI
TOLUENE ABSORPTION (CREMER)

λ IN ANGSTROMS	$\frac{1}{\lambda}$	ν_x	MEAN ν_x	INFRA-RED BANDS	
				Calc.	Obs.
ABH 2667.....	3749	298	3.36 μ	3.34 μ
2647.....	3778	269	271	3.69
AH 2635.....	3795	252	252	3.97	4.00
A 2630.....	3802	245	4.08
A 2615.....	3824	223	224	4.46
ABH 2603.....	3842	205	4.88
A 2600.....	3846	201	201	4.98
2595.....	3853	194	5.15	5.10
2589.....	3862	185	186	5.38	5.35
AH 2585.....	3869	178	5.62	5.51
A 2580.....	3877	170	5.88	5.80
2572.....	3888	159	6.29	6.20
AB 2567.....	3895	152	6.58	6.45
2565.....	3899	148	6.76	6.70
2560.....	3906	141	7.09	7.25
2554.....	3915	132	131	7.63	7.70
A 2550.....	3922	125	8.00	8.10
2541.....	3936	111	9.01
2539.....	3939	108	107	9.35	9.27
AB 2536.....	3943	104	9.61	9.73
H 2529.....	3954	93	10.75	10.60
2524.....	3961	86	86	11.60	11.15
2522.....	3965	82	12.20	12.03
2517.....	3974	73	13.70	13.78
B 2507.....	3988	59	61	16.39
2477.....	4037	10	10.5	95.24
H 2471.....	4037	0
A 2464.....	4058	11	10.5	95.24
2433.....	4110	63	61	16.39
BH 2420.....	4133	86	86	11.60	11.15
B 2407.....	4154	107	107.5	9.30	9.27
B 2394.....	4177	130	131	7.63	7.70
2359.....	4235	188	186	5.38	5.35
2354.....	4248	201	201	4.98
2341.....	4272	225	224	4.46
2326.....	4299	252	252	3.97	4.00
2315.....	4320	273	271	3.69

is again a good agreement between the observed and calculated values of the infra-red bands. The lettering of the lines has the

following meaning: The lines marked A are those which Cremer found to be the strongest, those marked B are the ones which form the heads of Cremer's series, while those marked H are the lines which Hartley considered to be the strongest.

It is of some interest to notice that the central line of toluene, 4047, is very nearly the same as that of benzene, 4055. As $4047 = 10 \times 405$ very nearly, so, as in the case of benzene, $9 \times 405 = 3645$ should be the central line of the fluorescence bands. If Dickson's values for the fluorescence of toluene be taken, it is clear that the maximum of 3650 must be the center of the system. Dickson's measurements of the maxima can be arranged as in Table XII,

TABLE XII
TOLUENE FLUORESCENCE (DICKSON)

λ in Angstroms	$\frac{1}{\lambda}$	ν_x
2886.....	3465	205 (205)
2809.....	3561	89 (86)
2740.....	3650	0
2676.....	3737	87 (86)
2646.....	3779	129 (132)
2622.....	3814	164 (159)

the figures in parentheses again showing the corresponding values of $\frac{\nu}{x}$ found in the absorption-band group. The accuracy of measurement of the wave-lengths of fluorescent maxima is not very great, and if the correction for the effect of solvent be applied there appears to be an error of 9 units in the value found for the central line. This, however, is well within the limits of experimental error.

p-XYLENE

Although the vapor absorption spectrum of *p*-xylene was investigated by Hartley, more accurate measurements have been published by Mies,¹ who showed that the fine lines can very readily be arranged in series. He observed in the spectrum a certain number of strong lines which he denoted by A, and also a number of slightly less strong lines which he denoted by B. The A and B lines form

¹ *Zeit. wiss. Phot.*, 7, 357, 1909.

two series with constant frequency differences. Then further he found other lines, the frequencies of which differ by definite amounts from the frequencies of the members of the A and B series. He thus established four series which he denoted by A, C, B, and D, the C and D series being connected with the A and B series respectively. In Table XIII are given the absorption lines of *p*-xylene

TABLE XIII
p-XYLENE ABSORPTION (MIES)

λ IN ANGSTROMS	$\frac{1}{\lambda}$	ν_x	MEAN ν_x	INFRA-RED BANDS	
				Calc.	Obs.
2814.....	3554	315	316	3.17 μ	3.25 μ
2800.....	3671	298	298	3.36	3.38
A 2785.....	3591	278	277.5	3.60
C 2771.....	3609	260	258	3.88
B 2757.....	3627	242	241	4.15
D 2744.....	3644	225	222	4.50
A 2722.....	3673	196	196.5	5.09
2717.....	3680	189	5.28	5.30
C 2709.....	3691	178	178	5.62
B 2695.....	3710	159	160	6.25	6.10
2691.....	3716	153	6.55	6.35
2685.....	3724	145	6.90	6.55
D 2682.....	3728	141	140.5	7.12	6.90
2680.....	3731	138	7.25	7.25
A 2664.....	3753	116	117	8.55	8.60
2661.....	3758	111	111	9.04	9.05
2657.....	3764	105	104	9.60	9.62
C 2650.....	3773	96	97	10.31	10.20
2643.....	3785	84	84	11.90	11.90
B 2637.....	3792	77	78	12.82	12.58
B 2584.....	3869	0
B 2533.....	3948	79	78	12.82	12.58
2530.....	3953	84	84	11.90	11.90
D 2521.....	3967	98	97	10.31	10.20
2517.....	3973	104	104	9.60	9.62
2512.....	3980	111	111	9.04	9.05
A 2508.....	3987	118	117	8.55	8.60
C 2494.....	4009	140	140.5	7.12	7.25
B 2483.....	4028	161	160	6.25	6.90
D 2471.....	4048	178	178	5.62	6.35
A 2460.....	4066	197	186.5	5.09	6.10
2447.....	4087	218	222	4.50
B 2434.....	4109	240	241	4.15
2425.....	4124	255	258	3.88
A 2412.....	4146	277	277.5	3.60
C 2400.....	4167	298	298	3.36	3.38
B 2389.....	4186	317	316	3.17	3.25

arranged with reference to the line $\frac{1}{\lambda} = 3869$ as center, and the letters refer to Mies's classification. Again every infra-red band is accounted for and the greater symmetry of the molecule is shown by the fact that out of the 14 infra-red bands 11 give rise to pairs of absorption lines.

The frequency of the central line $3869 = 15 \times 258$ almost exactly, and therefore $14 \times 258 = 3612$ should be the central line of the fluorescence. Only four fluorescence bands were observed by Dickson and the frequencies of these should arrange themselves around this as center. The four frequencies when corrected for solvent are 3504, 3584, 3665, and 3744, and these obviously may be arranged around 3624 as center as shown in Table XIV. Now

TABLE XIV
p-XYLENE FLUORESCENCE (DICKSON)

λ in Angstroms	$\frac{1}{\lambda}$	$\frac{1}{\lambda} + 13$	ν_x
2865.....	3492	3504	120 (117)
2801.....	3572	3584	40 (39)
2739.....	3653	3665	41 (39)
2681.....	3732	3744	120 (117)

$3624 = 14 \times 258.8$ and consequently the fundamental interval is very near that of the absorption-band system. The small number of the fluorescence bands makes it impossible to arrive at greater accuracy.

The absorption lines and fluorescence maxima may also be arranged in the same way for *o*-xylene and *m*-xylene and they are shown in Tables XV, XVI, XVII, and XVIII. In these tables certain lines are marked A or F. Those marked A are the lines which Hartley considered to be the heads of the sub-groups, while those marked F give the same values of ν_x as appear in the fluorescence spectrum. The wave-lengths are taken from Mies's paper.¹

The effect of the want of symmetry of the molecule is very well shown in Table XV as also in *m*-xylene. The frequency of the

¹ *Zeit. wiss. Phot.*, 8, 287, 1910.

TABLE XV
o-XYLENE ABSORPTION (MIES)

λ IN ÅNGSTRÖMS	$\frac{1}{\lambda}$	ν_x	MEAN ν_x	INFRA-RED BANDS	
				Calc.	Obs.
2777.....	3601	308		3.25 μ	3.25 μ
2770.....	3610	299		3.33	3.38
F 2730.....	3663	246		4.07	
F 2699.....	3705	204		4.90	
2691.....	3716	193		5.18	5.24
A 2683.....	3727	182		5.49	
A 2668.....	3748	161		6.21	6.20
2666.....	3751	158		6.33	6.30
2659.....	3761	148		6.74	{ 6.75 6.86
2654.....	3768	141	141	7.09	7.25
2650.....	3774	135		7.41	
A 2647.....	3778	131		7.63	
A 2633.....	3798	111		9.01	8.91
2628.....	3805	104		9.64	{ 9.50 9.78
2624.....	3811	98	97	10.31	10.20
F 2620.....	3817	92	91.5	10.91	
2607.....	3836	73	75	13.33	13.60
F 2572.....	3888	21		47.62	
A 2558.....	3909	0			
2509.....	3986	77	75	13.33	13.60
F 2500.....	4000	91	91.5	10.91	
2497.....	4005	96	97	10.31	10.20
2474.....	4042	141	141	7.09	7.25

central line $3909 = 13 \times 300.7$, and the next multiple is $12 \times 300.7 = 3608$, which may be taken as the center of the fluorescence bands. In Table XVI the frequencies of the fluorescence bands

TABLE XVI
o-XYLENE FLUORESCENCE (DICKSON)

λ in Angstroms	$\frac{1}{\lambda}$	$\frac{1}{\lambda} + 13$	ν_x
3135.....	3190	3203	405
3038.....	3292	3305	303 (299)
2986.....	3349	3362	246 (141)
2896.....	3453	3466	142 (141)
2798.....	3574	3587	21 (21)
2713.....	3686	3699	91 (91.5)
2680.....	3731	3744	141 (141)
2636.....	3794	3807	199 (204)
2603.....	3842	3855	247 (246)

are increased by 13 units in order to correct for the effect of the solvent. The central line 3864 is almost exactly 13×297 , and therefore $12 \times 297 = 3564$ should be the center of the fluorescence. Dickson found only three maxima of fluorescence and they all lie

TABLE XVII
m-XYLENE ABSORPTION (MIES)

λ IN ANGSTROMS	$\frac{I}{\lambda}$	ν_F	MEAN ν_F	INFRA-RED BANDS	
				Calc.	Obs.
2802.....	3569	295	3.39 μ	3.38 μ
2721.....	3675	189	5.29	5.25
F 2716.....	3682	182	181	5.52
2703.....	3699	165	163.5	6.12	6.20
2694.....	3712	152	6.58	6.77
F 2687.....	3722	142	142	7.04
2684.....	3726	138	7.25	7.25
2668.....	3748	116	8.62	8.70
2663.....	3755	109	9.17	9.17
2658.....	3762	102	103	9.70	9.68
2655.....	3767	97	10.30	10.20
2648.....	3776	88	87.5	11.43	11.42
2640.....	3788	76	74.5	13.42	13.20
F 2601.....	3645	19	20	50.00
2588.....	3864	0
F 2574.....	3888	21	20	50.00
2540.....	3937	73	74.5	13.42	13.20
2531.....	3951	87	87	11.43	11.32
2520.....	3968	104	103	9.70	9.70
F 2496.....	4006	142	142	7.04
2484.....	4026	162	163.5	6.12	6.20
F 2473.....	4044	180	181	5.52

on the ultra-violet side of 3564. If this be correct then, allowing 14 units for the effect of the solvent, the bands may be arranged as in Table XVIII. It is, however, manifestly impossible to draw any definite conclusions from only three maxima.

TABLE XVIII
m-XYLENE FLUORESCENCE (DICKSON)

λ in Angstroms	$\frac{I}{\lambda}$	$\frac{I}{\lambda} + 14$	ν_F
2802.....	3569	3583	19 (20)
2715.....	3683	3697	133 (142)
2685.....	3724	3738	174 (181)

There can be little doubt from the foregoing results that the conception of combining the frequencies of the short-wave infra-red bands with those of the central lines of the absorption and fluorescence bands is perfectly justified. The agreement between the calculated and observed values is remarkably good in every case.

The general conception can be put to a very severe test in the following way. Dickson found in the fluorescence spectrum of naphthalene 14 well-defined maxima which are very regularly arranged. In fact their frequencies may be expressed by the formula

$$\frac{1}{\lambda} = 3326 - 47.12 \times n,$$

where $n=0, 1, 2, \dots, 13$. He found small differences between the observed values and those calculated from the formula, especially in the case of the band with the smallest frequency. It would seem, therefore, that in making any calculations from the frequencies it would be preferable to use the values obtained from the formula. Now the absorption spectrum of naphthalene in the infra-red region has not been measured and the only fact known about it is that Coblenz found a band at 3.25μ for a solution of the compound in carbon tetrachloride. It is not possible, consequently, to check the values of frequency differences against infra-red measurements. Since the fluorescent bands are very symmetrically arranged it is possible accurately to calculate the frequency differences from that of the central line. This central frequency must be a multiple of the fundamental frequency, and the next higher multiple should form the center of the absorption band. From this new frequency, by making use of the frequency differences found in the fluorescent spectrum, it should be possible to calculate the frequencies of the lines in the ultra-violet absorption band.

In Table XIX are given the frequencies of the fluorescent maxima of naphthalene as corrected by Dickson and arranged symmetrically with respect to the mean frequency 3020, together with the frequency differences. The calculated values of the infra-red bands are given so that when this region is investigated the observed values may be compared.

Now the central frequency $3020 = 302 \times 10$, and as the fundamental frequency of naphthalene is 302, the central frequency of the absorption band should be $302 \times 11 = 3322$. In order to calculate the frequencies of the lines in the absorption-band group we thus use $3322 \pm \nu_x$, the values of ν_x being those given in Table XIX.

TABLE XIX
NAPHTHALENE FLUORESCENCE (DICKSON)

$\frac{1}{\lambda}$ Å	ν_x	Infra-Red Bands
2714.....	306	3.27 μ
2761.....	259	3.86
2808.....	212	4.72
2855.....	165	6.06
2902.....	118	8.48
2949.....	70.5	14.2
2996.....	23.5	42.6
3020.....	0
3043.....	23.5	42.6
3090.....	70.5	14.2
3138.....	118	8.48
3185.....	165	6.06
3232.....	212	4.72
3279.....	259	3.86
3326.....	306	3.27

The absorption of naphthalene vapor has been investigated by Purvis, who found that the band group shown by the alcoholic solution is not resolved into fine lines. It is necessary, therefore, to make use of the solution spectrum of naphthalene for the present comparison. This spectrum has been measured by several observers,¹ and Mr. F. C. Guthrie in my laboratory has kindly repeated the observations, using the new Hilger ultra-violet spectrophotometer, the accuracy of which far exceeds that of the old method of qualitative measurement.

In Table XX the first column shows the values of ν_x obtained from the fluorescence bands and given in Table XIX. The second column contains the calculated frequencies of the absorption bands, while the corresponding wave-lengths appear in the third column. In the fourth column are given Mr. Guthrie's measurements. No

¹ Hartley, *Chemical Society Transactions*, **39**, 153, 1881; **67**, 685, 1885; Baly and Tuck, *ibid.*, **93**, 1902, 1908; Purvis, *ibid.*, **101**, 1315, 1912.

correction for solvent is here needed since the fluorescence measurements were also made with a solution. The agreement between calculated and observed values is exceedingly good in view of the fact that there are no infra-red measurements against which the frequency differences (ν_x) can be checked. Certain of the calcu-

TABLE XX
NAPHTHALENE ABSORPTION

ν_x	$\frac{1}{\lambda}$	ABSORPTION BANDS IN A	
		Calc.	Obs.
306.....	3016	3311
259.....	3063	3265
212.....	3110	3215	3218
165.....	3157	3168	3158
118.....	3204	3121	3118
71.....	3251	3076
23.....	3299	3031	3025
0.....	(3322)
23.....	3345	2990	2965
71.....	3393	2945	
118.....	3440	2907
165.....	3487	2868	2867
212.....	3536	2828	2840
259.....	3581	2793	2798
306.....	3628	2757	2759
			2670

lated absorption bands do not appear in the solution spectrum and the broad band at 2965 does not seem to divide. One more absorption band has been observed at 2670 beyond those that have their counterpart in the fluorescence spectrum. It may be asserted that the foregoing calculation confirms the theory here put forward in a striking fashion.

Two interesting points may be noted, one of which is the agreement of the only observed infra-red band of naphthalene with the calculated value, and the other is the fundamental frequency of 302. This frequency is practically the same as that of *o*-xylene which is 301. Naphthalene can be looked upon as containing ortho-substituted benzene rings and it would seem, therefore, as if 301 or 302 might prove to be the fundamental frequency of ortho-disubstituted benzene compounds.

There is no doubt that it should also be possible on the present theory to explain the phosphorescent spectra as observed by von Kowalski¹ and Goldstein² with certain organic compounds. Both these authors investigated the phosphorescence of the solid substances at very low temperatures, but we have no knowledge of the shifts of the bands under these conditions as compared with the vapor. It is impossible to calculate the frequencies from these authors' measurements in the way adopted above.

The following substances may be taken, namely benzene and *p*-xylene, both of which were investigated by von Kowalski³ and the latter also by Goldstein. The fundamental frequencies of these compounds are 405 and 258, respectively. The simplest method of calculation is to find whether the phosphorescence maxima can be arranged in each case with reference to a multiple of the fundamental frequency, due regard being paid to the fact that the maxima are certain to be moved toward the red. The accuracy reached by these authors is only about 25 angstroms and therefore the frequencies are expressed with only three figures. But in spite of this it is clear that the same relation holds good here also.

Thus in benzene the frequencies of the phosphorescence maxima can be arranged symmetrically with respect to $\frac{1}{\lambda} = 242$ as shown in Table XXI, together with the values of ν_x (in parentheses) found

TABLE XXI
BENZENE PHOSPHORESCENCE (VON KOWALSKI)

$\frac{1}{\lambda}$	ν_x	$\frac{1}{\lambda}$	ν_x
230.....	12 (12.7)	263.....	21 (20.8)
233.....	9 (9.2)	270.....	28
239.....	3	274.....	32 (31.8)
242.....	0	280.....	38
249.....	7 (7.7)	284.....	42 (40.5)
252.....	10 (10.2)	289.....	47
260.....	18 (18.4)	295.....	53

¹ *Phys. Zeit.*, **12**, 956, 1911.

² *Ibid.*, **12**, 614, 1911; *Deutsch. phys. Gesell. Verh.*, **14**, 33, 493, 1912.

³ *Loc. cit.*

in the absorption band. It may be pointed out that the frequency of 47 corresponds very nearly to the infra-red band at 2.18μ ($\frac{1}{\lambda} = 46$).

We thus have for the fundamental frequency of Benzene the following values:

Phosphorescence.....	6×403.3
Fluorescence.....	9×405
Absorption.....	10×405

In the case of *p*-xylene the values given in Table XXII are obtained. It is possible that there is an error in von Kowalski's

TABLE XXII

PHOSPHORESCENCE (VON KOWALSKI)			CATHODOLUMINESCENCE (GOLDSTEIN)	
$\frac{1}{\lambda}$	ν_x	Mean ν_x	$\frac{1}{\lambda}$	ν_x
234.....	22	22 (22.2)	176.....	30 (29.8)
239.....	17	17.5 (19 and 16)	180.....	26 (26)
243.....	13	13.5 (13.8)	184.....	22 (22.2)
249.....	7	8 (7.8)	188.....	18 (19)
253.....	3	2.5	192.....	14 (14)
256.....	0		196.....	10 (10.5)
258.....	2	2.5	200.....	6 (5.9)
265.....	9	8 (7.8)	205.....	0
270.....	14	13.5 (13.8)	208.....	2
274.....	18	17.5 (16 and 19)	212.....	6 (5.9)
282.....	26	?	Central line 205.6	
Central line 256				

measurement of the last maximum on his list. We thus have the following values for the fundamental frequency of *p*-xylene:

Cathodoluminescence.....	8×257
Phosphorescence.....	10×256
Fluorescence.....	14×258
Absorption.....	15×258

Very great accuracy from the values of the phosphorescent maxima is not to be expected, since the measurement of these are far from accurate. There seems to be no doubt, however, that the same relations hold good with them as in the case of the ultra-violet band groups.

3. *Determination of the basis constants $\left(\frac{h}{2\pi^2 I}\right)$ from the known absorption in the short-wave infra-red region, and the calculation from these of the component lines in an ultra-violet absorption-band group.*—Although the extension of Bjerrum's conception to the ultra-violet absorption-band groups is completely successful, it must clearly be understood that the whole problem is by no means solved. For example, only about 30 out of the 200 absorption lines composing the ultra-violet absorption-band group of benzene have been accounted for. In the explanation of these 30 lines the short-wave infra-red bands only have been employed. It is true that practically all the known infra-red bands have been pressed into service, but there still remain the long-wave infra-red bands, that is to say those bands due to the rotational frequencies of the molecules. Nothing is known at present about the rotational frequencies of any one of the compounds dealt with above. If it were possible by some means to arrive at these values, then by combining these with the frequency of the central line it should be possible to calculate the frequency of every absorption line in any one absorption-band group.

The present position of the argument may be summed up as follows: There exists a constant difference between the frequencies of the central lines of absorption-, fluorescence-, and phosphorescence-band groups of any one compound, and, further, this constant difference equals the frequency of a band in the short-wave infra-red region. Bjerrum has shown that the structure of any one band group in the short-wave infra-red is explained by the combination of the central frequency of that band with the rotational frequencies of the molecules, which frequencies are given by the expression $\nu_r = \frac{nh}{2\pi^2 I}$. It has now been shown that it is possible to explain certain of the absorption lines in the ultra-violet and visible absorption-band groups and also the fluorescent- and phosphorescent-band groups by the combination of their central frequencies with the frequencies of the centers of the observed infra-red bands in the short-wave region. Is it now possible from a knowledge of the short-wave infra-red bands of any substance

alone to determine the value or values of $\frac{h}{2\pi^2 I}$ for that substance, and from these values to calculate the entire structure of the absorption-band groups of that substance in whatever region they occur? I may say that I have succeeded in doing this and furthermore in calculating the absorption of certain compounds from the values of $\frac{h}{2\pi^2 I}$ of their component radicles.

As already pointed out, Eucken showed that the infra-red absorption bands of water-vapor of longer wave-length than about $10\ \mu$ can be expressed by the Bjerrum formula; that is to say, their frequencies form consecutive multiples of two basis constants, $\frac{h}{2\pi^2 I}$ (he having assumed two degrees of freedom). If wave-length reciprocals are used, the values of these basis constants are 5.78 and 2.5, respectively. Eucken, however, entirely failed to explain the very remarkable variations in the intensities of the infra-red bands of water. He extended his series from the far infra-red only to $10.5\ \mu$ and offered no explanation of the extraordinary intensity of the bands at $6.0\ \mu$, $3.0\ \mu$, $2.0\ \mu$, and $1.5\ \mu$. It is in this respect that Bjerrum's theory is incomplete, for the whole essence of the theory is that the frequencies of the centers of the infra-red bands are consecutive multiples of one or more fundamental constants or bases. The theory in no way accounts for the fact that certain select multiples of the constants give rise to absorption bands which are far more intense than the neighboring multiples on each side.

On the other hand, if two basis constants are functionally active, then there must exist a convergence frequency of the two which is the least common multiple of the two. Such a convergence frequency will necessarily be especially active, since it is keyed with both series, and I suggest, therefore, that this is the reason why an infra-red absorption band is especially pronounced in intensity—namely that the frequency of the band is either the least common multiple of the two basis constants or is a multiple of that least common multiple. If this principle be accepted, it seems entirely to solve the difficulty connected with the intensity of

infra-red absorption bands and renders the calculation of the values of the basis constants relatively simple. This is adopted as the fundamental principle in all that follows.

The most intense absorption bands of water-vapor in the short-wave infra-red region lie at 6.25 , 6.0 , 3.0 , 2.0 , and 1.5μ , and the wave-numbers of these are 160.0 , 166.6 , 333.3 , 500.0 , and 666.6 , respectively. Eucken has pointed out that 2.5 is one of the basis constants of water, and the foregoing wave-numbers at once suggest that there is another basis constant of 6.6 . The first reciprocal, 160.0 , is an even multiple of these two constants, for $160 = 64 \times 2.5 = 24 \times 6.6$, while the second reciprocal, 166.6 , is the least common multiple of the two. The three remaining reciprocals are the least common multiple multiplied by 2, 3, and 4, respectively.

It is probable that the intensities of the absorption bands due to the multiples of the basis constants acting alone must decrease

as the value of n increases in the formula $\frac{nh}{2\pi^2 I}$, and consequently in the short-wave infra-red region, where n is large, the absorption bands due to these multiples acting alone will be very faint indeed. For instance, in the case of water-vapor no small absorption bands have been detected between the great bands given above. When, however, that frequency is reached which is either an even multiple or the least common multiple of the basis constants, then a very strong absorption band is evidenced. It follows further from this that in the case of water, for instance, the only possible regions of still shorter wave-length at which absorption bands can evidence themselves will be at frequencies which are multiples of 166.6 . There will, obviously, be found a constant frequency difference of 166.6 between such absorption bands, and a physical explanation is again found for the relation previously dealt with between the frequencies of the bands in the ultra-violet and visible regions and an infra-red band. It is also now clear why only one band in the infra-red is concerned.

From what has been proved before as regards the application of Bjerrum's theory to the structure of ultra-violet and visible absorption bands, it is clear that we are now in a position to calculate the region and the entire structure of any absorption band

of water-vapor. There are two basis constants, 2.5 and 6.6, and possibly a third, 5.78. In the first place, the central line of any absorption band must have a frequency which is some multiple of 166.6. In the second place, there will be symmetrically distributed on each side of this central line pairs of absorption lines due to the combination of the central frequency with consecutive multiples of 2.5, 5.78, and 6.6. The central line with maximum absorption will therefore have a frequency $\left(\frac{1}{\lambda}\right)$ of $166.6x$, and there will also occur pairs of absorption lines the frequencies of which will be given by $166.6x \pm nK_1$, $166.6x \pm nK_2$, and $166.6x \pm nK_3$, where x is some whole number, K_1 , K_2 , K_3 are 2.5, 5.78, 6.6, respectively, and $n=1, 2, 3$, etc. Again, it is to be expected that the absorption-band group will be divided into sub-groups and the frequencies of the heads of these sub-groups will be given by $166.6x \pm 160$, $166.6x \pm 166.67$, $166.6x \pm 333.33$, since 160, 166.67, and 333.33 are the frequencies of the most intense absorption bands in the short-wave infra-red region.

Unfortunately nothing is as yet known about the ultra-violet absorption band of water except that it would appear from refractivity measurements¹ to lie in the very extreme ultra-violet with a frequency of 10666.67 (64×166.6). Hence it is not possible to put the theory to the test of experiment in this case.

Attention may here be drawn to the influence of temperature on the width of absorption bands, it being a well-known fact that they become narrower with fall of temperature.² At the boiling-point of hydrogen it has been shown that the bands appear only as fine lines. The effect of temperature in all probability is to change the molecular rotational energy, and as the temperature falls the effective values of n in the formula $\frac{nh}{2\pi^2 I}$ become smaller in number, and indeed at very low temperatures only the lowest multiples of the basis constants will be active. Obviously the absorption bands will become narrower as the temperature falls,

¹ Baly, *Phil. Mag.*, **27**, 632, 1914.

² J. Becquerel, *Comptes rendus*, **144**, 420, 1907.

and at exceedingly low temperatures they may appear only as single lines, namely the central lines of the systems.

Although an experimental test of the theory cannot be applied in the case of water-vapor, there would be no such difficulty in the case of benzene, the ultra-violet absorption-band group of which has been investigated very completely. If, therefore, it is possible to find the basis constants of benzene from its known infra-red absorption, the experimental verification can easily be found in this compound. Coblentz has measured 20 absorption bands of benzene between the limits $1\ \mu$ and $13\ \mu$ and they differ very much among themselves in intensity. Of these bands the most pronounced appear at 9.78 , 6.75 , 5.5 , 3.25 , 2.48 , 2.18 , and $1.68\ \mu$. If the wave-numbers of all the infra-red bands of benzene are considered, it is at once apparent that they are very nearly multiples of 4, and it seemed at first sight that they could all be expressed with very fair accuracy as multiples of 4. It seems evident then that 4 is one of the basis constants of benzene. This, however, gives no explanation of the very remarkable intensity differences between the bands, and, further, all the consecutive multiples of 4 do not evidence themselves as bands even between 10 and $13\ \mu$, where perhaps they might be expected to appear.

Now the two most outstanding and characteristic bands of benzene are those at $6.75\ \mu$ and $3.25\ \mu$; they are characteristic in the sense that they generally appear in the absorption spectra of the simple derivatives of benzene. The wave-numbers of these two bands are almost exactly 148 and 307.6 and on the least-common-multiple principle they are the least common multiples of 4 and 3.7, and 4 and 7.6, respectively. Consequently these three basis constants explain the two most characteristic bands of benzene.

Again, these three constants also explain some of the other important bands the frequencies of which are whole multiples of two of the three constants. Thus $7.6 \times 24 = 4 \times 46 = 184$, which is the wave-number of $\lambda = 5.43\ \mu$, a value very close to Coblentz' measurement of $5.50\ \mu$. Then also $7.6 \times 60 = 4 \times 115 = 460$, the wave-number of $\lambda = 2.174\ \mu$, a value exceedingly close to Coblentz' measurement of $2.18\ \mu$. Further, the wave-number of $6.75\ \mu$ is 148 , and $2 \times 148 = 296$, the wave-number of $3.37\ \mu$, which is hidden

in the great band at 3.25μ , while $3 \times 148 = 444$, the wave-number of 2.25μ , which is hidden in the band at 2.18μ ; but $4 \times 148 = 592$ is the wave-number of 1.68μ , the value actually measured by Coblenz. The three basis constants of 3.7, 4, and 7.6 therefore explain all the important absorption bands of benzene between 1μ and 13μ except those at 2.48μ and 9.78μ . As regards the former, it is remarkable that the component absorption lines of the ultra-violet band group of benzene can be symmetrically arranged around the frequency of 4050 as center. This value is 10×405 which is very near the wave-number of 2.48μ . Again, no combination of the three foregoing basis constants gives a number near this value, and since it appears to be a fundamental one for benzene it is in all probability due to the existence of a fourth basis constant of 10.125. The least common multiple of 4 and 10.125 is 405, the wave-number of 2.49μ , a value exceedingly close to that measured by Coblenz, 2.48μ .

We are left with the band at 9.78μ , which, however, does not appear to be a specially characteristic band of benzene in spite of its intensity, since it does not evidence itself with any definiteness in benzene derivatives. This band and the remainder of less intensity are doubtless due to multiples of the four basis constants which happen to lie near together with the result that their effectiveness as absorbers is enhanced. Thus 10×10.125 gives a band at 9.88μ , and 3.7×28 gives a band at 9.54μ , and the mean of these is 9.76μ . Added to this, the other two bases give bands in the immediate neighborhood which tend still further to enhance the intensity. All the remaining bands can be accounted for in the same way by the fact that multiples of two of the constants happen to lie near together. It is interesting to note that when two such multiples are not very close a weak and broad absorption band is shown.

The entire short-wave infra-red band system of benzene can thus be accounted for by the existence of four basis constants. Again, it is evident that no absorption band of any importance can be exhibited by benzene with a shorter wave-length than 1μ except at a frequency which is some multiple of the least common multiple of two of the basis constants. If, therefore, the approxi-

mate position of the ultra-violet absorption band of benzene be known, it should now be possible to calculate the wave-numbers of all the component absorption lines of that group. It happens to be peculiarly simple owing to the symmetry of the benzene molecule which results in a very obvious symmetry of the absorption-band group. The wave-number of the central line of the system is undoubtedly $10 \times 405 = 4050$, and the wave-numbers of the component lines can then be computed from

$$4050 \pm 3.7n, 4050 \pm 4.0n, 4050 \pm 7.6n, 4050 \pm 10.125n.$$

The reciprocals of the wave-numbers thus obtained will give the wave-lengths, but these must be corrected for the refractive index of air before they can be compared with the observed values. In Table XXIII is given the complete list of absorption lines in the red side of the ultra-violet band group of benzene and in the ninth column are to be found their wave-lengths corrected for the refractive indices of air. In the last two columns are given the values observed by Hartley and by Grebe. The agreement between the calculated and observed values is very close and thoroughly justifies the theory here put forward. All the calculated wave-lengths have not as yet been observed, but this is not surprising as so many of them lie very close together. It would seem from Hartley's paper that there exist more lines than were actually distinguished by him. He recorded a great number of narrow absorption bands which were resolved on some of his negatives and not on others. The general conclusion may be drawn from the measurements of these bands that other lines exist beyond those specifically mentioned by Hartley. The wave-lengths of the lines in the blue side of the band have also been calculated and the agreement between the observed and calculated values is equally good. There is therefore no need for their reproduction.

Reference has been made previously to the division of the benzene band into sub-groups, and the opinion was expressed that the heads of these sub-groups are due to the combination with the central frequency of the frequencies of the short-wave infra-red bands. As there seems to be some doubt about Hartley's measurements of these heads—that is to say, as regards which lines are

TABLE XXIII

ULTRA-VIOLET ABSORPTION BAND OF BENZENE

$$K_1=3.7, K_2=4.0, K_3=7.6, K_4=10.125$$

Red Side of the Band

m_1	$\frac{1}{\lambda}$	m_2	$\frac{1}{\lambda}$	m_3	$\frac{1}{\lambda}$	m_4	$\frac{1}{\lambda}$	λ Calc.	λ Obs. Hartley	λ Obs. Grebe
0.	4050.0							2468.4	2469	2468.3
1.	4046.3							2470.7		
		1	4046.0					2470.9		2471
2.	4042.6							2471.9	2472	
				1	4042.33			2473.1		
		2	4042.0					2473.4		
						1	4039.875	2474.7	2474	2474.5
3.	4038.9							2475.2		
		3	4038.0					2475.8	2476	2476
4.	4035.2							2477.5	2477	
				2	4034.67			2477.8		
		4	4034.0					2478.2	2479	2478.6
5.	4031.5							2479.7	2480	2480
		5	4030.0					2480.7		
						2	4029.750	2480.8	2481	2481.1
6.	4027.8							2482.0	2482	
				3	4027.00			2482.5		
		6	4026.0					2483.2	2483	2483
7.	4024.1							2484.3	2484	2484.7
		7	4022.0					2485.6	2485	
8.	4020.4							2486.6	2486	
						3	4019.625	2487.1	2487	
				4	4019.33			2487.3		
		8	4018.0					2488.1		2488.3
9.	4016.7							2488.9	2489	
		9	4014.0					2490.6	2490	
10.	4013.0							2491.2	2491	2491
				5	4011.67			2492.0	2492	
		10	4010.0					2493.1	2493	
						4	4009.500	2493.4		2493.7
11.	4009.3							2493.5		
		11	4006.0					2495.6	2495	
12.	4005.6							2495.8	2496	2496.3
				6	4004.00			2496.8	2497	
		12	4002.0					2498.0		
13.	4001.9							2498.1	2498	
						5	3999.375	2499.5	2499	2499.1
		13	3998.0					2500.0		
14.	3998.2							2500.4	2501	2501
				7	3996.33			2501.6	2502	
15.	3994.5							2502.7		
		14	3994.0					2503.0	2503	
16.	3990.8							2505.1	2505	2504.4
		15	3990.0					2505.6		
						6	3989.250	2506.0	2506	2506.3
				8	3988.67			2506.4		
17.	3987.1							2507.4	2407	
		16	3986.0					2508.2	2509	

TABLE XXIII

n_1	$\frac{1}{\lambda}$	n_2	$\frac{1}{\lambda}$	n_3	$\frac{1}{\lambda}$	n_4	$\frac{1}{\lambda}$	λ Calc.	λ Obs. Hartley	λ Obs. Grebe
18..	3983.4	17	3982.0	9	3981.00	7	3979.125	2509.7	2510	2510.4
19..	3979.7	18	3978.0	10	3973.33	8	3969.000	2510.6	2511.2	2512
20..	3976.0	19	3974.0	11	3965.67	9	3958.875	2512.0	2512	2512
21..	3972.3	20	3970.0	12	3958.00	10	3948.750	2512.4	2513	2515.5
22..	3968.6	21	3966.0	13	3950.33	11	3938.625	2513.2	2514.5	2516
23..	3964.9	22	3962.0	14	3942.67	12	3928.500	2514.4	2515.6	2517.8
24..	3961.2	23	3958.0	15	3935.00	13	3918.375	2516.0	2516	2518.2
25..	3957.5	24	3954.0	16	3927.33	14	3912.00	2516.7	2517	2518.8
26..	3953.8	25	3950.0	17	3919.67	15	3905.000	2518.2	2518	2519.1
27..	3950.1	26	3946.0	18	3912.00	16	3897.000	2518.8	2519	2520.1
28..	3946.4	27	3942.0	19	3904.33	17	3889.000	2520.7	2521	2520.1
29..	3942.7	28	3938.0	20	3896.67	18	3881.000	2520.9	2522	2522
30..	3939.0	29	3934.0	21	3889.00	19	3873.000	2521.4	2523	2523.3
31..	3935.3	30	3930.0	22	3881.33	20	3865.000	2523.8	2524	2524.5
32..	3931.6	31	3926.0	23	3873.67	21	3857.000	2525.3	2525	2525.3
33..	3927.9	32	3922.0	24	3866.00	22	3849.000	2525.8	2526.5	2526.0
34..	3924.2	33	3918.0	25	3858.33	23	3841.000	2526.1	2528	2528
35..	3920.5	34	3914.0	26	3850.67	24	3833.000	2528.4	2529	2530
36..	3916.8	35	3910.0	27	3843.00	25	3825.000	2528.5	2531	2531
37..	3913.1	36	3906.0	28	3835.33	26	3817.000	2530.7	2532	2532.1
		37	3902.0	29	3827.67	27	3809.000	2530.9	2533	2533
		38	3898.0	30	3820.00	28	3801.000	2531.7	2534	2534
		39	3894.0	31	3812.33	29	3793.000	2533.3	2535	2536.2
		40	3890.0	32	3804.67	30	3785.000	2533.5	2536	2536.2
		41	3886.0	33	3797.00	31	3777.000	2535.7	2538	2538
		42	3882.0	34	3789.33	32	3769.000	2536.1	2538	2538
		43	3878.0	35	3781.67	33	3761.000	2538.0	2539	2539.6
		44	3874.0	36	3774.00	34	3753.000	2538.3	2540	2540.6
		45	3870.0	37	3766.33	35	3745.000	2538.6	2541	2541.3
		46	3866.0	38	3758.67	36	3737.000	2540.4	2542.8	2542.4
		47	3862.0	39	3751.00	37	3729.000	2540.6	2543	2544
		48	3858.0	40	3743.33	38	3721.000	2541.3	2544	2544
		49	3854.0	41	3735.67	39	3713.000	2542.8	2547	2547.3
		50	3850.0	42	3728.00	40	3705.000	2543.8	2549	2549
		51	3846.0	43	3720.33	41	3697.000	2544.8	2550	2550
		52	3842.0	44	3712.67	42	3689.000	2545.2	2551	2551
		53	3838.0	45	3705.00	43	3681.000	2545.5	2552	2552.1
		54	3834.0	46	3697.33	44	3673.000	2546.4	2554	2554.2
		55	3830.0	47	3689.67	45	3665.000	2547.6	2555	2555.5
		56	3826.0	48	3682.00	46	3657.000	2549.0	2556	2556.8
		57	3822.0	49	3674.33	47	3649.000	2550.0		
		58	3818.0	50	3666.67	48	3641.000	2550.5		
		59	3814.0	51	3659.00	49	3633.000	2551.4		
		60	3810.0	52	3651.33	50	3625.000	2551.6		
		61	3806.0	53	3643.67	51	3617.000	2552.4		
		62	3802.0	54	3636.00	52	3609.000	2554.2		
		63	3798.0	55	3628.33	53	3601.000	2554.8		
		64	3794.0	56	3620.67	54	3593.000	2555.5		
		65	3790.0	57	3613.00	55	3585.000	2556.8		

TABLE XXIII—Continued

n_1	$\frac{I}{\lambda}$	n_2	$\frac{I}{\lambda}$	n_3	$\frac{I}{\lambda}$	n_4	$\frac{I}{\lambda}$	λ Calc.	λ Obs. Hartley	λ Obs. Grebe
38..	3909.4							2557.2	2557	
						14	3908.250	2558.0		2558.0
		36	3906.0					2559.5		
39..	3905.7			19	3904.33			2559.6	2559.5	2560
								2560.5	2561	
40..	3902.0	37	3902.0					2562.1	2562	
41..	3898.3							2564.4		
		38	3898.0			15	3898.125	2564.5		
				20	3896.67			2564.6	2565	
42..	3894.6							2565.5	2566	2565.5
		39	3894.0					2566.9	2567	
43..	3890.9							2567.2		2568
		40	3890.0					2569.3	2569	
				21	3889.00			2569.9		
						16	3888.000	2570.5		
44..	3887.2							2571.2	2571	
		41	3886.0					2571.7	2572	
45..	3883.5							2572.6		2572.4
		42	3882.0					2574.2		
				22	3881.33			2575.2		
46..	3879.8							2575.6		
		43	3878.0					2576.6	2576.5	2576.7
						17	3877.875	2577.8		
47..	3876.1							2578.0	2578	
		44	3874.0					2579.1	2579	2579
				23	3873.67			2580.5	2580.5	
48..	3872.4							2580.7		
		45	3870.0					2581.6	2582	2581.9
49..	3868.7							2583.2	2583	
						18	3867.750	2584.0	2584	
		46	3866.0	24	3866.00			2584.7	2585	2585
50..	3865.0							2585.9	2586	
		47	3862.0					2586.5	2587	2587.0
51..	3861.3							2588.5	2588.5	
				25	3858.33			2589.0		2589
		48	3858.0					2591.0	2591	
52..	3857.6					19	3857.625	2591.2		
		49	3854.0					2591.5		
53..	3853.9							2593.9		2592.9
				26	3850.67			2594.0	2594	
54..	3850.2							2596.1	2596	
								2596.5		
		50	3850.0					2596.6	2597	
						20	3847.500	2598.2	2598	2597.8
55..	3846.5							2598.9		2599
		51	3846.0					2599.3	2600	
				27	3843.00			2601.3	2601	2601.3
56..	3842.8							2601.4		
		52	3842.0					2602.0	2602	
57..	3839.1							2604.0	2604	2603.9
		53	3838.0					2604.7		
						21	3837.375	2605.1	2605	2605

TABLE XXIII—Continued

n_1	$\frac{I}{\lambda}$	n_2	$\frac{I}{\lambda}$	n_3	$\frac{I}{\lambda}$	n_4	$\frac{I}{\lambda}$	λ Calc.	λ Obs. Hartley	λ Obs. Grebe
58..	3835.4	28	3825.33	2606.5	2606	...
...	...	54	3834.0	2607.5	2608	...
59..	3831.7	2609.0	...	2609.3
...	...	55	3830.0	2610.2	2610	...
60..	3828.0	29	3827.67	2611.5	2611.5	...
...	22	3827.250	2611.8
...	...	56	3826.0	2612.0	...	2612.4
61..	3824.3	2612.9	2613	...
...	...	57	3822.0	2613.1
62..	3820.6	30	3820.00	2615.6	2615	2614.7
...	2616.6	2616	2616
...	...	58	3818.0	23	3817.125	2617.0	2617	...
63..	3816.9	2618.3	2618	...
...	...	59	3814.0	2618.9	2619	...
64..	3813.2	31	3812.33	2619.1
...	...	60	3810.0	2621.1	2621	2621.1
...	2621.8
65..	3809.5	2622.3	...	2623
...	2623.8	2624	...
66..	3805.8	61	3806.0	24	3807.000	2624.2	2625	...
...	32	3804.67	2626.0	2626	2625.4
67..	3802.1	2626.6
...	...	62	3802.0	2627.5	2628	...
68..	3798.4	2629.3	2629	2629
...	...	63	3798.0	2629.4
...	33	3797.00	25	3796.875	2631.9	2632	2631.6
69..	3794.7	2632.1
...	...	64	3794.0	2632.9	2633	2633
70..	3791.0	2634.4	2634	2634.4
...	...	65	3790.0	2734.9	2635	...
...	34	3789.33	2637.0	2636	...
71..	3787.3	2637.7	2637	...
...	26	3786.750	2637.2
...	...	66	3786.0	2639.6	2639	2639
72..	3783.5	2640.0
...	...	67	3782.0	2640.4	2641	...
...	35	3781.67	2642.2	2642	2642
73..	3779.9	2643.5	2644	...
...	...	68	3778.0	2643.6
...	2644.8	2645	...
74..	3776.2	27	3776.625	2646.1	2646.5	2646.2
...	...	69	3774.0	36	3774.00	2647.1
75..	3772.5	2647.3	2647.5	...
...	...	70	3770.0	2648.9
76..	3768.8	2650.0	2650	2650.5
...	2651.7	2652	...
...	2652.6	2653	...
...	37	3766.33	28	3766.500	2654.2
...	...	71	3766.0	2654.3	2654	...
77..	3765.1	2654.5
...	...	72	3762.0	2655.2	2655	2655.2
...	2657.4

TABLE XXIII—Continued

n_1	$\frac{I}{\lambda}$	n_2	$\frac{I}{\lambda}$	n_3	$\frac{I}{\lambda}$	n_4	$\frac{I}{\lambda}$	λ Calc.	λ Obs. Hartley	λ Obs. Grebe
78..	3761.4			38	3758.67			2657.8		2658.2
		73	3758.0					2659.7	2659.5	
79..	3757.7					29	3756.375	2660.2		
80..	3754.0	74	3754.0					2660.4		
81..	3750.3			39	3751.00			2661.3	2662	
82..	3746.6	75	3750.0					2663.1	2664	2663
		76	3746.0					2665.1	2665	
				40	3743.33			2665.6		
83..	3742.9	77	3742.0			30	3746.250	2665.9	2666	2665.9
84..	3739.2	78	3738.0					2668.3		
				41	3735.67	31	3736.125	2668.5	2668.5	
85..	3735.5	79	3734.0					2668.7	2669	
86..	3731.8	80	3730.0					2670.6	2670.5	
87..	3728.1	81	3726.0	42	3728.00			2670.9	2671	
		82	3722.0			32	3726.000	2671.6	2672	2671.8
88..	3724.4							2673.6		
89..	3720.7	83	3718.0	43	3720.33			2674.4	2675	
90..	3717.0	84	3714.0			33	3715.875	2675.8		
91..	3713.3	85	3710.0	44	3712.67			2676.1	2676	
92..	3709.6	86	3706.0					2676.2	2677.5	2676.9
93..	3705.9			45	3705.00	34	3705.750	2677.3		
		87	3702.0					2678.9	2680	
94..	3702.2	88	3698.0	46	3697.33			2680.2	2681.5	
95..	3698.5					35	3695.625	2681.5	2681.5	
96..	3694.8	89	3694.0					2681.6	2683	2684.1
97..	3691.1	90	3690.0	47	3689.67			2684.2	2684.5	
								2685.9		
								2686.9		
								2687.1	2687	
								2688.8	2689	2688.9
								2689.6	2690	
								2690.4	2691	
								2691.7		
								2692.2	2692	
								2692.7		
								2694.6	2694	2694
								2694.9	2695	
								2697.5		
								2697.6	2697	
								2697.7		
								2698.2	2698	2699
								2700.3	2700	2700
								2700.4		
								2703.0	2703	
								2703.4		
								2703.8		
								2705.1		2705
								2705.7	2706	
								2706.3		
								2708.4	2708	
								2709.2	2709	
								2709.5	2709.5	

TABLE XXIII—Continued

n_1	$\frac{I}{\lambda}$	n_2	$\frac{I}{\lambda}$	n_3	$\frac{I}{\lambda}$	n_4	$\frac{I}{\lambda}$	λ Calc.	λ Obs. Hartley	λ Obs. Grebe
98..	3687.4							2711.1		
		91	3686.0					2712.1		
						36	3685.500	2712.5	2713	
99..	3683.7							2713.9	2714	
		92	3682.0	48	3682.00			2715.1	2715	
100..	3680.0							2716.6		
		93	3678.0					2718.1	2718	
101..	3676.3							2719.3	2719	
						37	3675.375	2720.0		
				49	3674.35			2720.8		
		94	3674.0					2721.0		
102..	3672.6							2722.1		
		95	3670.0					2724.0		
103..	3668.9							2724.8		
				50	3666.67			2726.5	2726	
		96	3666.0					2727.0		
104..	3665.2					38	3665.250	2727.5		
		97	3662.0					2729.9		
105..	3661.5							2730.3		
				51	3659.00			2732.2	2732	
		98	3658.0					2733.0		
106..	3657.8							2733.1		
						39	3655.125	2735.1	2735	
107..	3654.1	99	3654.0					2735.9	2736	
				52	3651.33			2737.9	2738	
108..	3650.4							2738.6		
		100	3650.0					2738.9	2739	
109..	3646.7							2741.4	2741	
		101	3646.0					2741.9		
						40	3645.000	2742.7	2743	
				53	3643.67			2743.7		
110..	3643.0							2744.2	2744	
		102	3642.0					2744.9	2745	
111..	3639.3							2747.0	2747	
		103	3638.0					2748.0	2748	
				54	3636.00			2749.5		
112..	3635.6							2749.8		
						41	3634.875	2750.3		
		104	3634.0					2751.0		
113..	3631.9							2752.6		
		105	3630.0					2754.0	2754	
				55	3628.33			2755.3		
114..	3628.2							2755.4	2756	
		106	3626.0					2757.0	2757	
						42	3624.750	2758.0		
115..	3624.5							2758.2		
		107	3622.0					2760.1		
116..	3620.8							2761.8		
				56	3620.67			2761.9	2761	

the most intense in the sub-groups—it has seemed advisable to repeat these observations. Messrs. A. Williams and F. G. Tryhorn have very kindly measured for me the absorptive power of an alcoholic solution of benzene with the Hilger ultra-violet spectrophotometer. When corrected for solvent the frequencies of the heads of the sub-groups agree with those calculated from the short-wave infra-red bands. The correction for solvent in this region is about 18 units in the values of $\frac{1}{\lambda}$. The values are given in Table XXIV.

TABLE XXIV

Infra-Red Bands	ν_{μ}	$\frac{1}{\lambda}$	$\frac{1}{\lambda} - 18$	λ Calc.	λ Obs.	λ Obs. Hartley
3.25 μ	308	3724	3706	2685	2685	2682
4.40.....	227	3823	3805	2632	2630	2630
4.90.....	204	3846	3828	2612	2614
5.43.....	184	3866	3848	2599	2600	2600
9.78.....	102	3948	3930	2445	2540	2539
Center.....	0	4050	4032	2460	2462	2460
11.6.....	85	4135	4117	2429	2429	2426.5
5.43.....	184	4231	4216	2372	2376	2376
4.40.....	227	4283	4265	2345	2344
3.25.....	308	4358	4340	2304	2300
2.18.....	460	4510	4492	2228	2230

In the first two columns of the table are given the wave-lengths and wave-numbers of the infra-red bands, in the third column are given the wave-numbers of the corresponding lines in the ultra-violet group, while in the fourth column these values are corrected for solvent. The wave-lengths of these lines are to be found in the fifth column, and Williams and Tryhorn's measurements of the heads of the sub-groups in the sixth column. I also append Hartley's values for a benzene solution in the last column. The agreement between observed and calculated values leaves no doubt that the sub-groups are due to the principal short-wave infra-red bands and the combination of their frequencies with that of the central line.

4. *Calculation of the absorption lines of phenol from the basis constants of water and benzene and of aniline from those of ammonia and benzene.*—The infra-red absorption of a very large number of compounds has been investigated by Coblentz and one outstanding

conclusion can be drawn from his work, namely that the characteristic infra-red bands of a substance are also to be found in the spectra of its simple derivatives. Thus the benzene bands at 3.25 and 6.75μ are also exhibited by a number of its derivatives. Again, the absorption bands of water are shown by salts with water of crystallization, and, moreover, at least one of these is shown by compounds containing the hydroxyl group. This at once suggests that in the spectrum of a compound there is some additive function of the spectra of its constituents. The existence of such an additive function can be tested in the case of phenol which is a derivative of benzene and water, for both of which we now know the values of the basis constants.

Coblentz did not investigate the absorption of phenol over the entire region from 1μ to 13μ , but he found three very strong bands at 2.97 , 6.25 , and 6.75μ . It is fairly obvious that the first of these is the water band at 3.0μ and is therefore due to the basis constants of water, namely 2.5 and 6.6 , while the band at 6.75μ is due to the benzene basis constants 3.7 and 4.0 . On the other hand, the wave-number of $\lambda = 6.25 \mu$, namely 160 , is a whole multiple of each of the three basis constants 4 , 2.5 , and 6.6 ,* for $160 = 4 \times 40 = 2.5 \times 64 = 6.6 \times 24$. Water shows two bands at 6.25μ and 6.0μ , and of these the wave-number of the first is the only one that is a multiple of a benzene basis constant as well as of those of water. Obviously, therefore, this band will be enormously enhanced in the case of phenol. It is thus clear that the three infra-red absorption bands of phenol, of which that at 6.25μ is the strongest, can be entirely accounted for by the basis constants of its component radicles benzene and water, for one is due to basis constants of benzene alone, one is due to the basis constants of water alone, while the third is due to those of water and benzene combined.

From these facts the absorption-line system of the ultra-violet band group can be at once calculated, since it is evident that the central frequency of such a band group must be a multiple of 160 , the wave-number of the only infra-red phenol band that is due to the combined constants of benzene and water. It may be noted in passing that this is confirmed by the fact that phenol in solution

shows a constant difference of 160 between the wave-numbers of its absorption and fluorescent bands as already shown in the earlier part of this paper. Now Purvis and McClelland¹ have measured the wave-lengths of the component absorption lines of one of the ultra-violet absorption-band groups of phenol, and these all lie between the limits 2812 and 2500 angstroms. The only multiple of 160 which possibly can be the central wave-number of the system is $24 \times 160 = 3840$. I have therefore calculated the wave-numbers of the absorption lines from

$$3840 \pm 2.5n, 3840 \pm 3.7n, \text{ and } 3840 \pm 4.0n,$$

and the corresponding wave-lengths, corrected to their values in air, are given together with Purvis and McClelland's measurements in Table XXV. I have used two of the basis constants of benzene and one of those of water, because phenol is undoubtedly an aromatic compound; that is to say, its benzenoid properties are far more pronounced than those of a derivative of water. Attention may be drawn to the manner in which the absorption lines group themselves and to the fact that Purvis and McClelland have measured in most cases those lines which mark the heads of those groups. Although the observed lines are very much fewer in number than those calculated, yet all the former coincide with closely situated groups of lines, which groups, since they would not be resolved with the dispersion employed, would appear as single lines. The agreement between the observed and calculated values is very good and fully justifies the conclusion that the basis constants of benzene and water are acting independently. Some insistence may be laid on the fact that the entire absorption spectrum of phenol has thus been calculated from the infra-red spectra of benzene and water, no modification whatever being required in the fundamental constants of these two substances when combined in their compound phenol. The calculations for the beginning only of the red side of the band are given. The results obtained for the remainder of the red side and for the blue side are equally good.

Many other examples of this principle of the combination of the basis constants might be given, but it is only in relatively few cases

¹ *Chemical Society Transactions*, 103, 1088, 1913.

that the result can be tested on the ultra-violet absorption-band groups, since relatively few substances show these groups subdivided into fine lines.* Indeed this very fact is in agreement with the

TABLE XXV
ULTRA-VIOLET ABSORPTION BAND OF PHENOL

$$K_1=2.5, K_2=3.7, K_3=4.0$$

Red Side

n_1	$\frac{1}{\lambda}$	n_2	$\frac{1}{\lambda}$	n_3	$\frac{1}{\lambda}$	λ Calc.	λ Obs. Purvis
0	3840.0					2603.4	2603
1	3837.5					2605.1	2604
		1	3836.3			2605.9	
				1	3836.0	2606.1	
2	3835.0					2606.7	2607
3	3832.5	2	3832.6			2608.5	
				2	3832.0	2608.8	
4	3830.0					2610.2	
		3	3828.9			2610.9	2611
				3	3828.0	2611.6	
5	3827.5					2511.8	
		4	3825.2			2613.5	2613
6	3825.0					2613.6	
				4	3824.0	2614.7	
7	3822.5					2615.3	
		5	3821.5			2616.0	
8	3820.0			5	3820.0	2617.0	
		6	3817.8			2618.5	2618
9	3817.5					2618.7	
				6	3816.0	2619.8	
10	3815.0					2620.5	
		7	3814.1			2621.0	
11	3812.5					2622.2	
				7	3812.0	2622.5	
		8	3810.4			2623.6	2623
12	3810.0					2623.9	
				8	3808.0	2625.2	2625
13	3807.5					2725.5	
		9	3806.7			2626.1	
14	3805.0					2627.3	
				9	3804.0	2628.0	2628
		10	3803.0			2628.7	
15	3802.5					2629.0	
16	3800.0			10	3800.0	2630.7	2630
		11	3799.3			2631.3	2631
17	3797.5					2632.5	
				11	3796.0	2633.6	
		12	3795.6			2633.9	2634
18	3795.0					2634.3	2635
19	3792.5					2636.0	
				12	3792.0	2636.3	
		13	3791.9			2636.4	

theory, since the more complicated is a molecular system, the greater the number of basis constants, and hence the greater the number of lines packed together within the limits of one absorption-band group. The closer these lines lie together the less likely are they to be resolved, and hence the condition is soon reached when no such resolution is possible.

The principle of combination also holds good in the cases of aniline and toluene, for the ultra-violet band group of aniline can be accurately calculated from the basis constants of benzene and ammonia, and that of toluene from the constants of benzene and an aliphatic hydrocarbon. Coblenz investigated the infra-red spectra of a number of aliphatic hydrocarbons and found them all to be strikingly similar. As it is probable that normal hexane was examined in the state of greatest purity, this may be taken for the present purpose. It shows three very strong bands at $\lambda = 3.43$, 6.86 , and 13.8μ . The wave-numbers of these are very nearly multiples of 4 and the most probable values are 288, 144, and 72, respectively. Since these three bands are so intense in relation to all the others of these hydrocarbons, it may be concluded that there is a second basis constant of 7.2, of which the foregoing wave-numbers are multiples as well as of 4. These two basis constants explain all the intense infra-red absorption bands of the aliphatic hydrocarbons and it is very interesting that one of these, 4, is the same as in the case of benzene, which suggests that it is characteristic of a carbon chain.

Further evidence can now be gained as to the principle of combination in the spectrum of a compound of the basis constants of its component radicles. Thus myricyl alcohol shows very strong bands at 2.97, 3.43, 6.86, and 13.88μ . Of these no doubt the last three are due to the basis constants of the hydrocarbon chain, while the first is due to those of water. Again, triethylamine shows the hydrocarbon bands at 3.43, and 6.86μ , and also the ammonia bands at 6.1 and 9.3μ .

The infra-red spectrum of aniline shows bands at 2.97, 3.25, and 6.1μ , and of these the first and third are clearly due to the basis constants of ammonia, and the second to those of benzene. The same is true in the case of toluene, for it shows strongly the

benzene band at 6.75μ and the hydrocarbon bands at 6.86 and 13.88μ . There is also a single deep band at 3.34μ , and there is little doubt that this is due to the superposition of the benzene band at 3.25μ and the hydrocarbon band at 3.47μ . These four compounds again support the principle of combination, and in the two last cases the matter can be tested on the ultra-violet absorption system.

Owing to the complexity of the infra-red spectrum of ammonia it becomes somewhat difficult directly to determine the fundamental frequency of aniline, of which the central frequencies of the ultra-violet bands are multiples. On the other hand, aniline in solution shows two absorption-band groups, and at very small concentration¹ the frequencies of the centers of these bands are 3496.7 and 4355 , respectively. From these two measurements it is possible to calculate the most probable value of the fundamental infra-red frequency, for we have $x\nu_x = 3496.7$ (1), $y\nu_x = 4355$ (2), and $(y-x)\nu_x = 758.3$ (3), where x and y are integers and $y-x$ is small. It would seem obvious that the only possible values for x and y are 23 and 28, respectively, for the value of ν_x is then found to be 152.03 , 151.97 , and 151.65 from (1), (2), and (3); respectively. Now Purvis² has measured the wave-lengths of the component lines of the less refrangible ultra-violet band group of aniline and has recorded a strong absorption line at $1/\lambda = 3496.1$. This value may obviously be taken as a more accurate measurement of the central frequency than that obtained from the solution. The true value of ν_x or the fundamental infra-red frequency of aniline is therefore $3496.1/23 = 152.0$.

Now the principal basis constant of benzene is 4, and $38 \times 4 = 152$, and it would seem therefore that 3.8 must be one of the basis constants of ammonia. If this be so, then many of the infra-red absorption bands of ammonia must occur at frequencies which are multiples of 3.8. This is shown to be the case in Table XXVI, for eleven out of the sixteen ammonia bands between 3μ and 14μ are thus accounted for.

¹ The values for a very dilute solution are the same as for the vapor, a fact that will be dealt with in a further paper.

² *Chemical Society Transactions*, 97, 1546, 1910.

The agreement shown in this table would certainly justify the conclusion that 3.8 is the principal basis constant of ammonia.

TABLE XXVI

Factors	$\frac{I}{A}$	λ Calc.	λ Obs. Coblentz
19×3.8.....	72.2	13.85 μ	13.7 μ
22×3.8.....	83.6	11.96	11.98
23×3.8.....	87.4	11.44	11.43
25×3.8.....	95.0	10.53	10.4
27×3.8.....	102.6	9.75	9.9
28×3.8.....	106.4	9.40	9.3
30×3.8.....	114.0	8.77	8.9
40×3.8.....	152.0	6.58	6.51
43×3.8.....	163.4	6.12	6.1
45×3.8.....	171.0	5.85	5.8
88×3.8.....	334.4	2.99	2.98

It is now possible to calculate the wave-lengths of the component lines of the ultra-violet absorption-band group of aniline, and I have done this, using the central frequency 3496.1 and, as in the case of phenol, the two benzene constants 3.7 and 4.0, together with that now found for ammonia, namely 3.8. The following formulae were therefore used:

$$3496.91 \pm 3.7n, \quad 3496.1 \pm 3.8n, \quad \text{and} \quad 3496.1 \pm 4.0n,$$

and the results agree exceedingly well with those observed by Purvis and by Koch.¹

I have also calculated the wave-lengths of the absorption-band group of toluene, using the four basis constants 3.7, 4.0, 7.2, and 7.6, the central line being taken as the same as that of benzene. The latter is justified both by the fact that the absorption-band group of toluene is in exactly the same region as that of benzene, and also by the fact that so many absorption lines of toluene are the same as those of benzene. The agreement between the observed and calculated values is again exceedingly good and there is no need for the detailed reproduction of the calculations for aniline or toluene.

These results seem entirely to confirm the view put forward in the latter pages of this paper, that it is possible to calculate all

¹ *Zeit. wiss. Phot.*, 9, 401, 1910.

the absorption bands and their component lines from the infra-red absorption bands of the substance, and, further, that the absorption of compounds of two radicles throughout the whole spectrum from extreme ultra-violet to extreme infra-red is compounded from the infra-red absorption of the two radicles.

The whole position may be summed up as follows: Every system of molecules possesses certain basis constants, which according to Bjerrum represent the molecular rotational frequencies and are derived from the expression $\frac{h}{2\pi^2 I}$ where I is the moment of inertia and h the Planck constant, there being at least two values of I for each type of molecule. Absorption bands exist in the long-

wave region of the infra-red with frequencies equal to $\frac{nh}{2\pi^2 I}$, where $n=1, 2, 3$, etc. As the values of n increase, the intensity of the resulting absorption bands decreases and the effective values of n depend on the temperature of the substance. Convergence frequencies of the two series of basis constants exist and these form centers of bands in the short-wave infra-red region. No strong absorption band can be exhibited by any compound at shorter wave-length than 3μ , which is due to a single multiple of one basis constant. All absorption bands beyond 3μ must be due either to the convergence of two or more series of basis constants or to a multiple of such convergence frequency. There exists, therefore, a constant difference between the centers of such absorption bands, and this difference must equal such convergence frequency. Every absorption band, whether in the ultra-violet, visible, or short-wave infra-red region, consists of a central line the frequency of which is a convergence frequency or a multiple of that convergence frequency. Symmetrically distributed on each side of the central line are pairs of absorption lines, each pair being due to the combination of the central frequency with a basis constant according to the expression $C \pm nK$, where C is the frequency of the central line, K is a basis constant, and $n=1, 2, 3$, etc. The ultra-violet or visible absorption-band group may be divided into sub-groups and in such case the heads of the sub-groups are due to the combination with the central frequency of

those frequencies which are sufficiently active to give bands in the short-wave infra-red region. The same also holds good for fluorescence and phosphorescence spectra. Finally, in the case of a compound of two radicles the basis constants are the same as those of the two radicles. Every one of the foregoing deductions from the theory has clearly been proved to be true by experiment.

Although the present theory has been developed in two directions, it must be clearly understood that neither argument is complete without the other. In the first section of this paper the existence of molecular force fields is dealt with. These are opened by the effect of various solvents to different stages, each stage being characterized by its power of absorbing definite light vibrations. The theory therefore establishes the fact that a given molecular force field must possess certain definite free periods of vibration, and that these periods may be latent or called into play by the use of suitable solvents. These vibration periods may evidence themselves as the centers of either absorption, fluorescence, or phosphorescence bands. Although it is clear that the absorbed light must again be emitted at some frequency which is characteristic of the molecular system, the force-field theory does not carry us beyond the foregoing position and offers no explanation of the relation between the frequencies of ultra-violet and infra-red absorption bands.

On the other hand, the energy relations based on the energy-quantum theory show that there must exist a constant difference between the centers of successive absorption, fluorescent, and phosphorescent bands shown by a single substance and that this difference must equal the frequency of an infra-red band of that substance. They further show that all the free vibration periods possessed by a substance can be derived from two or more basis constants, but they do not explain why certain of these vibration periods in the ultra-violet and visible regions are active and why some of them are latent.

It may fairly be claimed that a combination of the two branches gives a reasonably complete theory of absorption, fluorescence, and phosphorescence, a theory which seems amply to be confirmed by experiment.

5. *Summary and conclusions.*—(1) The electromagnetic fields surrounding the atoms, used by Humphreys to explain the Zeeman and the pressure-shift effects, have been applied to molecules. The free and independent existence in a molecule of such atomic fields must be a metastable condition. There must ensue a condensing together of the force lines to form a molecular field, with the escape of energy.

(2) The chemical properties of a molecule must depend on the closed field of the molecule. If the field be entirely closed, the molecule will have no reactivity, and if after the maximum possible condensation has taken place there be left an uncompensated residuum, the molecule will possess residual affinity.

(3) The closed molecular fields can be opened by the influence of other molecules possessing residual affinity, an equilibrium between opened-up and non-opened-up molecules being established. The chemical reactivity will depend on this equilibrium.

(4) A second method of opening the closed fields is by the influence of light. The light shifts the equilibrium between the opened-up and non-opened-up molecules toward the reactive or opened-up side, a new photodynamic equilibrium being established. The light therefore does work on the system and is selectively absorbed.

(5) The force field of a complex molecule is itself complex and consists of a network of potential gradients which are attacked and opened in turn by the use of suitable solvents. Stages must therefore exist in the opening-up process.

(6) Each stage will be characterized by its power of selectively absorbing definite light waves and can be recognized in this way. Each stage thus represents a vibration period of the molecular system.

(7) The light energy absorbed must again be emitted at some frequency which is characteristic of the system. In most cases this frequency lies in the infra-red region, but in certain cases a portion of the energy is emitted in the visible or ultra-violet region when fluorescence or phosphorescence is manifested. Fluorescence and phosphorescence therefore mean the emission of energy with a frequency characteristic of the molecular system.

(8) Experimental proof is found in three sets of observations: first, by the existence of intermediate phases in chemical reactions, which phases represent higher stages in the opening up of the molecular force fields and are recognized by their power of absorbing light of longer wave-length; secondly, by the variation in absorptive power with progressive dilution of the solution; thirdly, by the fact that the fluorescence emission of certain organic compounds in one solvent has the same wave-length as the light absorbed by the same compounds in a second solvent.

(9) The frequencies of the centers of all the absorption, fluorescence, and phosphorescence bands shown by a substance are multiples of the frequency of an absorption band in the short-wave region of the infra-red. This is proved by the existence of a constant difference between the centers of successive band groups, whether absorption, fluorescence, or phosphorescence, and by the fact that this constant difference equals the frequency of an absorption band shown by the same substance in the short-wave infra-red region. Further proof is found in the fact that the refractivities of gases can be calculated from Sellmeyer's formula in which for the frequency of the theoretical absorption band there is substituted a multiple of a measured infra-red band.

(10) The structure of absorption-, fluorescent-, and phosphorescent-band groups is partly due to the combination of the central frequency with the frequencies of the short-wave infra-red absorption bands according to the formula $C \pm \nu_x$, where C is the central frequency and ν_x the frequencies of the short-wave infra-red absorption bands.

(11) The entire absorption, fluorescence, and phosphorescence, in whatever region they may lie, may be calculated from the molecular frequencies. According to Bjerrum these rotational frequencies are given by the expression $\frac{nh}{2\pi^2 I}$, where h is the Planck constant, I is the moment of inertia, and $n = 1, 2, 3$, etc. There are at least two basis constants $\left(\frac{h}{2\pi^2 I}\right)$ for every complex molecule.

(12) The successive multiples of the basis constants give rise to absorption bands in the long-wave infra-red region. Convergence

frequencies of two or more series of basis constants or multiples of such convergence frequencies give rise to absorption bands in the short-wave infra-red region. Multiples of these convergence frequencies give rise to the bands in the visible and ultra-violet regions.

(13) By combination of these convergence frequencies or their multiples with the successive multiples of the basis constants according to the formula $C = nK$, where K is a basis constant, all the component lines of any band group may be calculated. This has been done for the ultra-violet absorption-band group of benzene and the values show exceedingly close agreement with those observed.

(14) Where an absorption band shows subdivision into sub-groups, the heads of the sub-groups are due to the combination of the central frequency with those multiples of the basis constants which are sufficiently active to evidence themselves as absorption bands in the short-wave infra-red region.

(15) The absorption bands in the infra-red and all the component lines of the ultra-violet absorption-band groups of a compound of two radicles can be calculated from the basis constants of the two radicles. This is proved by the calculation of the absorption lines of phenol from the basis constants of benzene and water, and the absorption lines of aniline from those of benzene and ammonia.

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ON THIELE'S "PHASE" IN BAND SPECTRA

By H. S. UHLER

Several years ago, at the suggestion of Professor H. Kayser, the author undertook to test Thiele's hypotheses concerning emission band spectra by investigating their applicability to the third cyanogen band and the various "tails" which have been associated with it by King, Jungbluth, and others. The first part of the work, which was primarily experimental, has been completed by R. A. Patterson in collaboration with the writer. The second part of the problem would be purely arithmetical and would consist in unraveling the various series pertaining to the λ 3883 band by the aid of Thiele's methods and formulae. In the attempt to lay out a systematic plan for the computations, the difficulty of obtaining the numerical value of the phase c presented itself as apparently insuperable. That this difficulty has also appeared formidable to other investigators may be seen from the following quotations.

A. S. King¹ writes: ". . . and some of the constants used, notably n , the series-number of a selected line, are very hard to determine in the case of band spectra." Again: "Finding it impracticable to use Thiele's formulae, owing to the difficulty in determining the constants, I have tried to find some numerical relation. . . ." R. T. Birge² says: "It contains eight undetermined coefficients and so is very difficult to work with. . . . I have preferred to use simply Deslandres' Law. . . ." As far as the author has been able to find out, by a careful search through so much of the literature of the subject as is accessible to him, Thiele is the only investigator who has calculated the numerical values of c and of the remaining parameters involved in his formula. Since this state of affairs exists, as a good deal of importance is attached to the problem by Kayser and other writers, and since the author has succeeded in working out a method for evaluating c for any given band spectrum, he feels justified in publishing the results

¹ *Astrophysical Journal*, 14, 325, 326, 1901.

² *Ibid.*, 39, 72, 1914.

of his investigation, in spite of the fact that the processes involved are very elementary and now seem perfectly obvious. In this paper, therefore, it will be shown (a) precisely what Thiele's formulae and hypotheses mean from a purely mathematical point of view, (b) how to calculate the "phase" c for any band whose wave-lengths can be determined to a sufficiently high degree of accuracy, and (c) what conclusions may be drawn from the special cases to which the new method has been applied.

Thiele has stated his hypotheses very clearly in the following words:

The single established fact in the present theory of series, the only one which my investigations have more and more tended to confirm, is that the law which expresses the wave-length λ of the lines of a series as a function of the series-number n of the lines must have the form

$$\lambda = f[(n+c)^2] \quad (1)$$

where c is a constant, which I shall call the phase of the series. . . . Taking this law as a fundamental hypothesis, I accept all of its consequences. . . . The most important consequence of our hypothesis, $\lambda = f[(n+c)^2]$, is that it is necessary to take into account not only the lines corresponding to positive values of n , but also those obtained when $n < 0$. In other words a series must in general be composed of two groups of lines, each of which would ordinarily be called a series. I prefer to put it that the positive branch of each series must be accompanied by a negative branch of the same series, having the same head and the same tail and being represented alternately by a line in each interval of the other branch. These two branches may exactly coincide, in which case the phase of the series must be either $c=0$ or $c=\frac{1}{2}$ (evidently c must be defined so as to include only fractions properly so called).¹

That Thiele considers c to be rigorously and not approximately constant is emphasized in his second paper on this subject where he says: "That the phase must remain constant in each series is my fundamental hypothesis."²

Theoretically the phase c may be determined in three different ways for any given spectrum. One method consists in assuming a particular form of function in equation (1) and then evaluating the constants or parameters by repeated comparison of the calculated wave-lengths with the experimental data. In general, this

¹ *Astrophysical Journal*, 6, 66, 67, 1897.

² *Ibid.*, 8, 5, 1898.

process (which is the one used by Thiele in his analysis of the carbon band at λ 5165) requires the determination of the values of all of the parameters simultaneously. This fact is advantageous or just the reverse according as one needs to know all of the constants or as one desires to study the behavior of some parameter alone, such as c . When the function is complicated, or involves a relatively large number of independent literal coefficients, the labor of computing their values becomes very great. This is the discouraging feature of the equation used by Thiele,¹ namely:

$$\lambda = \lambda_0 - \kappa \left(\frac{n+c}{10} \right)^2 \cdot \frac{1 + s_1 \left(\frac{n+c}{10} \right)^2 + \dots + s_{r-1} \left(\frac{n+c}{10} \right)^{2r-2}}{1 + t_1 \left(\frac{n+c}{10} \right)^2 + \dots + t_r \left(\frac{n+c}{10} \right)^{2r}} \quad (2)$$

Furthermore, the process of "trial and error" would usually be extended over the entire length of the band under investigation and, when this is the case, it would yield mean values of the literal coefficients. Under these circumstances small but true variations in a hypothetical constant, such as c , might escape detection.

A second method of calculating c would be to substitute a sufficient number of experimental wave-lengths in the chosen function to make it possible, theoretically at least, to eliminate from the resulting equations of condition all of the parameters save the one required. If this scheme were feasible, it would afford an excellent means of testing some of Thiele's hypotheses. For example, comparison of the values obtained by calculating c from groups of selected wave-lengths at different places along one band series would show whether the phase is or is not a true constant, within the limits set by the probable errors of the experimental data. In general, however, it is not advantageous to make use of a process which requires the function to be *exactly* satisfied by the wave-lengths in a group. For, unless the number of data in a set were large, an anomalous line or a wave-length having a large error might alter the value of a small constant very appreciably. Both of the methods just outlined would give c if wave-lengths belonging exclusively to one and the same branch (positive or negative) of a

¹ *Astrophysical Journal*, 8, 10, 1898.

series were used in the computation. The value of c thus obtained would predict the wave-lengths of the conjugate branch (negative or positive respectively) and indicate the positions of the lines of one branch relative to those of the associated branch.

Although the second method suggested for the determination of the phase seems very promising in many respects, nevertheless it is not practicable. This statement is made advisedly because a great deal of time was wasted by the writer in trying to derive a working formula for c before he happened to hit upon the third method, which will be explained in later paragraphs. If the number of terms in equation (2) be restricted so that it may be written as

$$\lambda = \frac{a_0 + a_2(n+c)^2}{1 + b_2(n+c)^2},$$

and if for λ and n respectively the four wave-lengths M, N, P, Q , and the corresponding ordinals m, n, p, q , be substituted, elimination of a_0, a_2 , and b_2 will lead to a quadratic in c which is readily reducible to the form given by Thiele,¹ namely:

$$(m+n+p+q+4c)^2 = (m-n+p-q)^2 + \frac{4(m-q)(n-p)}{1 - \frac{M-N}{M-P} \cdot \frac{P-Q}{N-Q} \cdot \frac{m-p}{m-n} \cdot \frac{n-q}{p-q}}.$$

This formula is unsatisfactory in practice because it is liable to give incorrect results, primarily as a consequence of the small number of wave-lengths involved. For example, when the latest wave-lengths of four good lines of the singlet series between the first and second heads of the third cyanogen band ($M=3880.999, N=3879.964, P=3878.303, Q=3876.843, m=15, n=18, p=22, q=25$) were chosen at random and substituted in the last equation, it was found that $4c+80 = \pm 85.0345$ or $c = 1.2586$, which is incorrect because c must be less than unity. [Of course, c can be changed to 0.26 by increasing m, n, p , and q each by 1 since the left member of the equation has to maintain a constant sum for $m+n+p+q+4c$, the right side involving differences only. The spectrograms show, however, that $m=15$.] If, with $m=15, -0.002$ and $+0.002$ be added to M and Q , respectively, it follows that $4c+80 = \pm 81.6747$

¹ *Ibid.*, 6, 70. 1897.

or $c = 0.4187$, which illustrates how sensitive the quadratic may be to slight changes in the wave-lengths. If the wave-lengths satisfy an equation of the form

$$\lambda = a + \beta n + \gamma n^2$$

(which is approximately exact near the head of a band), it is easy to show that Thiele's quadratic leads to $m+n+p+q+4c = \pm \left(m+n+p+q + \frac{2\beta}{\gamma}\right)$, so that the required root, $c = \frac{\beta}{2\gamma}$, is independent of the value of m . Far from the beginning of a series the quadratic in c becomes altogether useless. For illustration, from the series chosen for the last numerical example let the following data be taken, namely $M = 3678.098$, $N = 3666.852$, $P = 3653.455$, $Q = 3642.477$, $m = 151$, $n = 156$, $p = 162$, and $q = 167$. Then $4c + 636 = \pm 271.4942$, that is, $c = -91.1264$ or -226.8736 and these roots are obviously meaningless.

Theoretically the next approximation to c can be obtained from the equation

$$\lambda = \frac{a_0 + a_2(n+c)^2 + a_4(n+c)^4}{1 + b_2(n+c)^2 + b_4(n+c)^4}.$$

Letting M, N, P, Q, R, S , denote wave-lengths and m, n, p, q, r, s , the corresponding series numbers, the equation for c becomes

$$| M(m+c)^4, (n+c)^4, P(p+c)^2, (q+c)^2, R, 1 | = 0.$$

Expanding the binomials and making use of the fact that a determinant having two (or more) identical columns vanishes, a complete sextic in c is obtained having 36 determinants, each of the sixth order, involved in its coefficients. If it were possible to transform this sextic so as to cause all of the wave-lengths to be present (preferably as binomial differences) in one term alone, as is the case with Thiele's quadratic, only one complicated coefficient would have to be evaluated in a given numerical case and the required root of the sextic might be obtained without too much labor by applying Horner's method of approximation. As a matter of fact

the coefficients of c^6 , c^5 , and c^4 may be reduced to 64Δ , $64\Delta \cdot \Sigma m$, and $16\Delta \left[(\Sigma m)^2 + \Sigma mn + \frac{\Delta'}{\Delta} \right]$ respectively, where

$$\Delta \equiv | M, 1, Pp^2, q^2, Rr, s |$$

and

$$\Delta' \equiv | M, 1, Pp^3, q^3, Rr, s |.$$

Division of all of the terms of the sextic by Δ still leaves an irreducible function of wave-lengths, namely $\frac{\Delta'}{\Delta}$, in the coefficient of c^4 . As might be expected, the literal coefficients become more involved as the power of c decreases.

In his study of the α , β , γ I, ϵ I, ϵ II, and ζ series of the carbon band at λ 5165, Thiele found it necessary to take $r=3$ in formula (2). To determine c by the elimination of the seven remaining parameters, eight wave-lengths would be required and an equation of the twelfth degree in c would have to be solved. The coefficients of this equation would involve 576 determinants, each of the eighth order, after all zero determinants had been culled out. It is therefore evident that the second general method proposed for finding the value of c is entirely out of the question. Furthermore, both of the methods suggested in the foregoing paragraphs are open to the objection that they require the assumption of some special type of function, such as formula (2), and hence may restrict the generality of the hypotheses associated with

$$\lambda = f[(n+c)^2].$$

The principle of the third method is perfectly general in so far as it depends solely upon Thiele's two fundamental hypotheses, namely: (a) only even powers of $n+c$ are involved in the function for λ , and (b) c is a constant for any one band series. More specifically, if $\lambda = f[(n+c)^2]$ be plotted in rectangular co-ordinates, the locus obtained will be symmetrical with respect to the straight line whose equation is $n = -c$ (\overline{AV} , Fig. 1). The two branches of an ideal Thiele band series (shaded off toward the shorter wave-lengths) would then have the general form of the curve BVF . The points of inflection correspond to the maximum first-differences of

wave-length approached in some bands and realized in the third cyanogen group. A straight line parallel to the axis of n , and at a suitable distance therefrom, will intersect the curve in two points, such as D and E . Hence, if n and n' denote (the algebraic values of) the abscissae of any two points on the curve which have the same value of λ , it follows at once that $c = -\frac{1}{2}(n+n')$. [$\overline{GH} = c$, $\overline{HE} = n$, $\overline{DH} = -n'$.] In the case of any series whose wave-lengths have been accurately determined there is no inherent difficulty associated with the calculation of n and n' corresponding to a chosen numerical wave-length. It is only necessary to evaluate the coefficients of

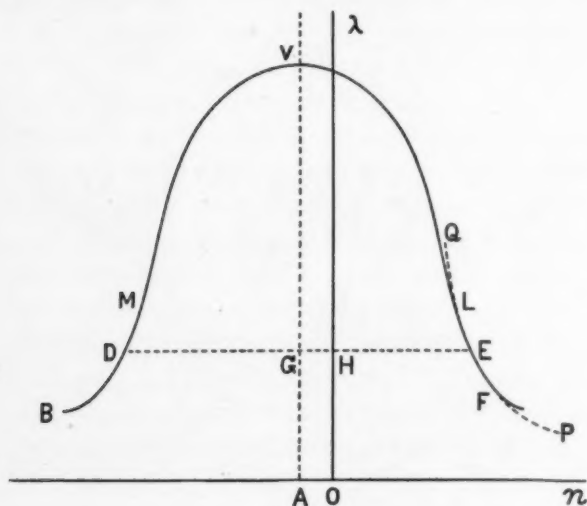


FIG. 1

any simple, convenient interpolation formula which represents a curve PQ fitting the locus of actual wave-lengths sufficiently closely over a limited range of spectral lines, such as FL or BM . In other words, the value of c may be obtained by taking an adequate number of terms of the power polynomial $\lambda = a_0 + a_1n + a_2n^2 + \dots + a_kn^k$, determining the coefficients, a_0, a_1, \dots, a_k from the known wave-lengths, substituting for λ an arbitrary wave-length (\overline{OH}), and solving for n . Then, using the same value of λ and repeating the process for the negative quadrant, the corresponding value of n' is computed. Knowing n and n' , c follows immediately

from the relation $c = -\frac{1}{2}(n+n')$. If the numerical data were perfect and Thiele's hypotheses correct, it would only be necessary to evaluate c for one value of λ , that is, for one pair of corresponding intervals on the two branches of the curve. If the hypotheses are rigorous but the wave-lengths slightly in error, several pairs of segments along the curve can be used and the mean of the slightly differing values of c formed. If, on the other hand, the general function $f[(n+c)^2]$ does not represent very closely a law of nature, the variations of c along the curve will bring this fact to light. Furthermore, the disadvantages arising from determining the coefficients of the interpolation formula by causing its curve to pass exactly through an equal number of experimental points may be avoided by making use of the method of least squares. By so doing, a comparatively small number of terms of the polynomial may be taken and the coefficients determined from a larger number of wave-lengths. In this way the influence of the unavoidable accidental errors of the experimental data will be minimized. In the present paper attention is focused primarily on the relative values of c at different places along a given series, and hence it is not necessary to know how many lines are comprised in the usually congested region of the head of a band or even if the band has a head of finite intensity. The difficulty of choosing between several values of c which are in a sense complementary is thus avoided. It is essential, of course, to number the lines of the same series consistently. Since, under these circumstances, relative ordinal numbers alone are of significance and since n and n' have opposite signs, it is always possible to transform the co-ordinates involved in the interpolation formula so as to use small ordinals (1, 2, 3, . . .) instead of the larger values (160, 161, 162, . . .) pertaining to the lines of long series.¹ This fact reduces enormously the labor involved in the calculation and solution of the "normal" equations.

The plan to be followed in the general case having been outlined, attention will now be directed to the details of the application of the method to numerical problems. As stated in an earlier paragraph, the equation

$$\lambda = a_0 + a_1 n + a_2 n^2 + \dots + a_k n^k$$

$$^1 c = -\frac{1}{2}[(n'+m) + (n-m)].$$

may be used to advantage as the interpolation formula. Before making any computations, however, it is necessary to find out how many terms of the polynomial will be sufficient. By actual trial the writer has found that the parabolic equation

$$\lambda = a_0 + a_1 n + a_2 n^2$$

gives perfectly satisfactory results. As a matter of fact this trinomial has worked so well that it was not deemed worth while to test an equation containing n^3 . It is not surprising that the parabolic formula is sufficient, in the case of band series, for two reasons. In the first place, the law of Deslandres holds very well near the head of a band and, for short intervals, it makes no appreciable difference whether wave-lengths or the reciprocals of wave-lengths ("frequencies") be used. Secondly, far away from the head (E and D , Fig. 1) the parabolic segments twine around the positive and negative branches of the $n\lambda$ curve in such a manner as to produce, at worst, a differential error in the calculation of c . In other words, the numerical values of n and n' corresponding to the same value of $\lambda(\overline{OH})$ are both larger or both smaller, by approximately equal amounts, when obtained from the interpolation parabolas than they would be if derived from the (unknown) equation of the series. Therefore the first-order differences practically cancel out in the expression for c , namely $-\frac{1}{2}(n+n')$. Moreover, for one parabola alone even the first-order divergence becomes negligible near the middle of the interval of wave-lengths employed in computing the normal equations.

As a concrete example, let the following wave-lengths, which Thiele has computed for the α series of the λ 5165 carbon band, be taken. (The object in using ideal wave-lengths instead of experimental data is to illustrate the manner in which the least-squares parabolas thread the curve given by formula (2) when the idiosyncrasies of the individual wave-lengths have been removed.)

In the first and second columns of Table I are given the series numbers used in the present calculation and by Thiele respectively, while the third column contains the wave-lengths computed by Thiele from formula (2). Instead of using the equation

$$\lambda = a_0 + a_1 n + a_2 n^2$$

just as it is written, the arithmetical work can be very appreciably reduced by replacing a_0 by $a' + \lambda'$, where λ' denotes the wave-length of a line at, or near, the middle of the group. The equations

TABLE I

n	" n "	λ_{ideal}	$\lambda_{\text{ideal}} - \lambda_{\text{parab.}}$
+1.....	+36	5003.278	+0.0044
2.....	37	4994.688	- .0043
3.....	38	4985.920	- .0049
4.....	39	4976.976	+ .0005
5.....	40	4967.864	+ .0041
6.....	41	4958.585	+ .0047
7.....	42	4949.146	-0.0045

of condition will then have only differences of wave-lengths for their constant terms, thus:

$$a' + n \cdot a_1 + n^2 \cdot a_2 = \lambda - \lambda'.$$

In the numerical example proposed $\lambda' = 4976.976$ and the equations of condition become

$$a' + 1a_1 + 1a_2 = +26.302$$

$$a' + 2a_1 + 4a_2 = +17.712$$

$$a' + 3a_1 + 9a_2 = + 8.944$$

$$a' + 4a_1 + 16a_2 = 0.000$$

$$a' + 5a_1 + 25a_2 = - 9.112$$

$$a' + 6a_1 + 36a_2 = -18.391$$

$$a' + 7a_1 + 49a_2 = -27.830$$

Hence, the first normal equation is

$$7a' + 28a_1 + 140a_2 = -2.375.$$

Much time and labor can be saved by solving a set of normal equations with literal coefficients and computing, once for all, the constants which do not involve the wave-lengths. Let the right-hand members of the three normal equations be symbolized by S , T , and U , respectively. ($S = -2.375$, $T = -262.158$, $U = -2075.900$, in the illustration.) The solutions may then be written as

$$a_1 = \frac{1}{\Delta} (s_1 S + t_1 T + u_1 U)$$

and

$$a_2 = \frac{1}{\Delta}(s_2 S + u_1 T + u_2 U).$$

a' may be found most conveniently by substituting the values of a_1 and a_2 in the first normal equation.

Since it is possible that other computers may desire to follow the method of calculating c suggested in this paper, the constants corresponding to 7, 8, 9, 10, 11, and k consecutive ordinal numbers have been collected in Table II. As implied above, the wave-lengths are to be numbered 1, 2, 3, Under these conditions

$$a' = \frac{1}{6k}[6S - 3k(k+1)a_1 - k(k+1)(2k+1)a_2].$$

In the concrete example

$$a' = +\frac{243 \cdot 147}{7}, \quad a_1 = -\frac{175 \cdot 2215}{21}, \quad a_2 = -\frac{1 \cdot 784}{21},$$

so that the point on the parabola corresponding to $n=4$ has the ordinate $\lambda_4 = \frac{104,516 \cdot 507}{21}$. The next step consists in calculating the coefficients of the parabolic equation pertaining to the lines whose series numbers are $-37, -38, \dots, -43$. When this has been accomplished the value of λ_4 is substituted for λ and the resulting quadratic in n' solved. In the case in question, the required root is $n' = -4.53173$; consequently $c = -\frac{1}{2}(-4.53173 + 4) = 0.26586$. The value of c used by Thiele in equation (2) was 0.266, hence the new method leads to a result which is too small by only 0.05 per cent. For practical purposes the agreement may be considered perfect. (The concordance might have been even better if Thiele's ideal wave-lengths had been recalculated.)

It is now appropriate to present the results obtained by applying the processes just explained to two independent sets of experimental data, namely, (a) the α and δ series of the λ 5165 carbon band calculated by Thiele, and (b) the series starting from the first head of the cyanogen band at λ 3883. In the first case it will be shown that c is not constant, and in the second, that the two series emanating from the head are not the positive and negative branches of the same series.

TABLE II

	7	8	9	10	11	k
s_1	-21,168	-51,408	-112,860	-228,690	-434,148	$-\frac{1}{120} k^2(k+1)^2(k-1)(k+2)(2k+1)$
t_1	+13,132	+28,560	+56,772	+105,105	+183,678	$+\frac{1}{180} k^2(k^2-1)(2k+1)(8k+11)$
u_1	-1,568	-3,024	-5,400	-9,075	-14,520	$-\frac{1}{12} k^2(k+1)^2(k-1)$
s_2	+2,352	+5,040	+9,900	+18,150	+31,460	$+\frac{1}{72} k^2(k+1)^2(k-1)(k+2)$
u_2	+196	+336	+540	+825	+1,210	$+\frac{1}{12} k^2(k^2-1)$
Δ	+16,464	+56,448	+166,320	+435,600	+1,038,180	$+\frac{1}{2160} k^3(k^2-1)^2(k^2-4)$

Since the wave-lengths at Thiele's disposal were not as accurate as the later values determined by Joseph Leinen,¹ use has been made of the more recent data in the computations. The second column of Table III contains the ordinal numbers assigned by Thiele to the spectral lines whose wave-lengths have been used by the author in computing the coefficients of the least-squares parabolas for segments of the positive branches of the series. The corresponding ordinals of the negative branches are given in the third column. Each value of c recorded in the fourth column was calculated from the two parabolas based on the data associated with the numbers in the same row and in the preceding columns.

TABLE III

Series	+ Branch-Ordinal Nos.	- Branch-Ordinal Nos.	c	Wave-Length Interval
$\alpha \dots$	+ 3,, + 9	- 3,, - 9	0.2632	5164.448-5153.380
$\alpha \dots$	+ 3,, + 9	- 4,, - 10	.2633	
$\alpha \dots$	+ 9,, + 16	- 9,, - 16	.2626	5155.740-5129.801
$\alpha \dots$	+ 9,, + 16	- 10,, - 17	.2625	
$\alpha \dots$	+ 20,, + 26	- 20,, - 22, - 24,, - 27	.2666	5116.003-5075.507
$\alpha \dots$	+ 36,, + 42	- 36,, - 42	.2684	5007.974-4944.885
$\alpha \dots$	+ 36,, + 42	- 37,, - 43	.2686	
$\delta \dots$	+ 8,, + 18	- 8,, - 18	.2499	5156.296-5119.417
$\delta \dots$	+ 23,, + 29	- 23,, - 29	.2417	5095.397-5052.823
$\delta \dots$	+ 35,, + 41	- 35,, - 41	.2375	5009.632-4951.622
$\delta \dots$	+ 52,, + 60	- 52,, - 57, - 59, - 60	0.2344	4843.180-4746.602

In three cases two parabolic equations for the negative branch were calculated in order to find out how much alteration in the value of c would be produced by a slight shift in the position of the negative interval with respect to a fixed region on the positive branch. As anticipated, the change in c is negligible, since it amounted to only 0.0002, or 0.075 per cent in the most unfavorable case. In the fifth and bottom rows of the table it will be noticed that lines -23 and -58, respectively, were omitted. This was done because the wave-lengths given by Leinen are displaced too far with respect to their neighbors to justify the inclusion of the data in the least-squares calculations. The numbers in the fourth column show conclusively that c is not strictly constant for the α and δ series of the λ 5165 carbon band. In the case of the α series the phase

¹ *Zeit. wiss. Phot.*, 3, 137, 1905.

increases from about 0.263 to 0.268 at least, while for the δ series it decreases from 0.250 to 0.235, or less. The values of c used by Thiele were 0.266 and 0.2445 for the α and δ series, respectively. As suggested in an earlier paragraph, it is probable that Thiele's method of computation would lead to a sort of integrated average value of the phase. This supposition is not inconsistent with the fact that the average of the extreme values 0.2625 and 0.2685 equals 0.2655, which happens to agree with 0.266 almost exactly. Likewise, for the δ series $\frac{1}{2}(0.2499 + 0.2375) = 0.2437$, which is only 0.33 per cent less than 0.2445. In this comparison the interval -52 to -60 was omitted because the wave-lengths of these faint lines were not at Thiele's disposal. In any event, the writer desires to lay special emphasis on the fact that the variations of c , as shown by the numbers in the fourth column of Table III, are real and not fictitious. In other words, these variations arise neither from the irregularities and small anomalies of the wave-lengths nor from the use of only three terms in the interpolation formula. Of the various crucial tests which have been made in this connection the following one is alone sufficient to remove all suspicion. The average (0.2629) of the first four values of c given in Table III was taken as standard, because the lines near the head of the band fit the parabolic interpolation formula very closely; and then the correction ϵ , which would have to be applied simultaneously to each and every one of the seven lines +36 to +42 to change c from 0.2686 to 0.2629, was calculated. In other words, ϵ denotes the displacement of the entire group of seven lines of the positive branch relative to the corresponding group (-37 to -43) of the negative branch, required to give $c = 0.2629$. It was found that $\epsilon = +0.104$ A, which is altogether too large to be accounted for on any reasonable basis. On the one hand, the wave-lengths cannot be *relatively* displaced by 0.1 A because one of the primary objects of Leinen's work was to determine their values as accurately as possible. He gives his experimental data to thousandths of an angstrom unit and hence the relative errors should not exceed 0.01 A at most. Moreover, the errors would not all be of the same sign. On the other hand, the parabolic equation used in the present computations cannot be responsible for the large value of ϵ because the

arithmetical sum of all the fourteen residuals ($\lambda_{\text{calc.}} - \lambda_{\text{obs.}}$), for both the positive and negative branches, amounts to 0.0927 Å, which is less than 0.104 Å. The just comparison, however, would be between 0.007 Å ($0.093 \div 14$) and 0.104 Å. These two numbers are not even of the same order of magnitude. By applying the same test to the δ series it was found that every one of the nine lines from +52 to +60 would have to be translated to shorter wave-lengths by 0.355 Å in order to change c from 0.2344 to 0.2499. The arithmetical sum of the eighteen residuals (inclusive of the anomalous value +0.052 Å pertaining to line -58) is 0.2918 Å, which is distinctly less than 0.355 Å. The average residual is only 0.016 Å instead of 0.355 Å.

Attention will now be turned to the series emanating from the first head of the cyanogen band at λ 3883. In this case, it will not be necessary to make use of wave-lengths given by other observers because the author has personally taken more than thirty negatives of this band in the third order of Rowland's best grating, which has 20,000 lines to the inch and a radius of curvature of about 21 feet. Moreover, some of the wave-lengths have been determined by the writer and all of the lines have been measured and studied very carefully by R. A. Patterson in this laboratory.

Judged by appearances, only two series start from the head near λ 3883. One series consists of doublets, which are very intense near the head, but which gradually decrease in strength until they fade out or get lost by superposition with lines of other series at the ordinal number 46. The other series (known as the Kayser and Runge series) starts out with single lines which are eventually resolved into close doublets. Under the experimental conditions, the lines of this series remain single beyond the more refrangible end of the doublet series first mentioned. The fact that the doublet series does not furnish data for the calculation of the phase beyond line 45 is very disappointing because the singlet series can be accurately measured to line 168. Moreover, it is rather unsatisfactory to be under the necessity of comparing resolved doublets with lines which are photographically single. The best that can be done is to calculate c from the axes of the single lines (positive branch) and the centers of each of the components

of the doublets taken as separate series (negative branches). Even under these unfavorable conditions it will be shown that the singlet and doublet series do not lead to constant values of c and hence do not constitute branches of single series according to Thiele's definition.

In order to show how extremely well the least-squares parabolas fit the experimental data, the results obtained by subtracting the observed values of the wave-lengths from the calculated numbers are given in Table IV (in the columns headed A). The wave-lengths corresponding to the parenthetical residuals were not used in the computations because the spectrograms indicate that the lines are either anomalous or confused with lines of other series. The bottom row contains the figures obtained by substituting the residuals in the usual formula for the probable error of a single observation. The subscripts ₁ and ₂ refer to the less and more refrangible components of the resolved doublets, respectively.

TABLE IV

n	A	n'	A	n'	A	n	A	n'	A
+15	-0.0024	-15 ₁	+0.0016	-15 ₂	-0.0006	+37	0.0000	-37 ₁	-0.0009
+16	+0.0025	-16 ₁	-0.0018	-16 ₂	+0.0008	+38	+0.0007	-38 ₁	+0.0003
+17	+0.0011	-17 ₁	+0.0004	-17 ₂	+0.0006	+39	-0.0001	-39 ₁	+0.0024
+18	-0.0006	-18 ₁	-0.0008	-18 ₂	0.0000	+40	-0.0024	-40 ₁	-0.0016
+19	+0.0006	-19 ₁	-0.0005	-19 ₂	-0.0013	+41	+0.0008	-41 ₁	-0.0007
+20	(-0.0096)	-20 ₁	+0.0004	-20 ₂	-0.0011	+42	+0.0024	-42 ₁	+0.0001
+21	-0.0010	-21 ₁	-0.0002	-21 ₂	+0.0025	+43	-0.0015	-43 ₁	(-0.0553)
+22	-0.0006	-22 ₁	+0.0018	-22 ₂	-0.0004	-44 ₁	+0.0003
+23	(+0.0045)	-23 ₁	-0.0006	-23 ₂	+0.0011
+24	-0.0006	-24 ₁	+0.0005	-24 ₂	-0.0030
+25	+0.0010	-25 ₁	-0.0008	-25 ₂	+0.0014
$e \dots$	± 0.0010	$e \dots$	± 0.0007	$e \dots$	± 0.0010	$e \dots$	± 0.0011	$e \dots$	± 0.0009

The value of the phase obtained from the groups +15, , +19, +21, +22, +24, +25, and -15₁, , -25₁ is 0.1667. The intervals +37, , +43 and -37₁, , -42₁, -44₁ give $c=0.1515$. In like manner the same groups of the positive branch combined with the sets -15₂, , -25₂ and -37₂, , -42₂, -44₂ lead to $c=0.0950$ and $c=0.1047$, in the order named. Hence, on receding from the first head of the band, the phase decreases for the less refrangible components of the doublets,

but increases for the components of shorter wave-length. The deviation from the mean is 4.8 and 4.9 per cent for the larger and smaller pairs of values of c respectively. In order to change the value of c from 0.1515 to 0.1667 all the lines of the group +37 to +43 would have to be displaced toward the shorter wave-length side by 0.025 Å, the set -37₁, , -42₁, -44₁, being looked upon as fixed. Similarly, a translation toward the red of 0.016 Å would have to be given to the entire group +37 to +43 in order to decrease the phase from 0.1047 to 0.0950, the set -37₂, , -42₂, -44₂ remaining stationary. If the lines of the branch which has been taken arbitrarily as positive (with no loss of generality, however) are really single, then the conclusion follows at once that the wave-length corrections are altogether too great to admit of the hypothesis that this series is related to the series of resolved doublets according to Thiele's method of combination. On the other hand, if the singlets are actually unresolved doublets, then two cases require consideration: (a) the less and more refrangible components of the discrete doublets are to be coupled with the less and more refrangible hypothetical components of the positive branch respectively; (b) the longer and shorter wave-length components of the resolved doublets correspond to the shorter and longer wave-length components of the unresolved series, in the order named. From general physical considerations case (a) seems to be the more reasonable. Moreover, Thiele himself combines the doublets of the λ 5165 band according to this plan. Under these conditions each of the numerical corrections 0.025 Å and 0.016 Å would have to be increased, thereby strengthening the evidence against the correlation of the positive and negative branches. On the other hand, it is only fair to examine the second possibility quantitatively.

In the first place, in the region between the first and second heads of the band the lines of the Kayser and Runge series are comparable in width with the components of the resolved doublets. If then the observed singlets are truly doublets, their hypothetical components must be extremely close together so that no sensible error can arise from treating the lines in question as if they were rigorously single. In other words, it is perfectly safe to consider

the phase values 0.1667 and 0.0950 as correct and to investigate the possible duality of the broader single lines of the set +37 to +43. According to the present calculations each of these lines should consist of a pair about 0.041 Å apart. The less refrangible component should lie on the longer wave-length side of the axis of the broad singlet and at a distance of 0.016 Å from this axis. Similarly the more refrangible component should be situated on the shorter wave-length side of the center of the unresolved singlet and at a distance of 0.025 Å from this center. Hence, the mean position of the hypothetical doublet would be displaced from the middle of the singlet by 0.0045 Å (toward the more refrangible edge). This hypothesis is untenable for several reasons, namely: (a) exposures of different lengths do not indicate any asymmetry in the singlets, (b) when the Kayser and Runge series eventually becomes resolved into doublets the components have sensibly equal widths and intensities, and (c) the residuals of the lines in question (see Table IV) show that the members of a group of seven or more lines cannot all be displaced in the same direction by as much as 0.0045 Å. The conclusion, therefore, that the singlet and doublet series starting from the first head of the λ 3883 cyanogen band do not form the positive and negative branches of a complete Thiele series is thoroughly justified.

In the cases of the α and δ series of the λ 5165 carbon band and the series from the chief head of the λ 3883 band, the only way left to make the phase constant is to assume either that $c=0$ or that $c=0.5$. These values of the phase mean that the lines of the series are made to coincide either with themselves or with the adjacent lines of the same series. Such a special arrangement is, of course, always possible. If it had been found that c was strictly constant and had a value different from 0 or 0.5 for a large number of bands, then self-conjugate series might occur in a relatively small number of cases as a consequence of special conditions in the radiating systems. Since, however, it has just been shown that c is not constant for the series examined, and since doubt is thereby thrown on the constancy of the phase for the remaining series computed by Thiele, the values 0 and 0.5 for c lose their significance as special cases and assume the aspect of artificiality. Conformable to strict logic

Thiele's hypotheses can be disproved in only two ways: by theoretical considerations based on the laws of radiation or by an examination of all bands capable of existence. From this point of view nothing can be done at the present time. On the other hand, in the opinion of the writer, the evidence adduced in the foregoing paragraphs throws enough doubt on certain of Thiele's hypotheses to require new evidence in their favor before they can be considered tenable.

In conclusion, a few additional comments will be appended which confessedly bear the imprint of personal opinion. Thiele's computations gave apparently constant values of the phase for two reasons, namely: (a) the method employed led to mean values of c , and (b) the agreement between the calculated and the experimental wave-lengths appeared satisfactory because the data at his disposal did not attain to the degree of accuracy which characterizes the more modern work. Moreover, a small error in c would constitute a still smaller percentage error in $n+c$, especially for the higher values of the ordinal n , and consequently formula (2) could reproduce the wave-lengths fairly well. No importance attaches to the fact that Thiele predicted the wave-lengths of faint lines which were found later by Leinen, because this could have been accomplished (with much less labor) just as well by extrapolation with a power series, involving only five terms,¹ for the positive and negative branches taken separately as natural series. The constancy of c , within the limits given above, is nothing more than the analytical expression of the well-known fact, pointed out by Deslandres, that series starting from the same head of a band run approximately parallel courses. Formula (2) owes its flexibility to the fact that it is the most general rational, algebraic function of even degree in $n+c$. Doubtless Thiele chose this form because, in general, the curve possesses a point of inflection and is asymptotic to the "tail" wave-length

$$\lambda_t = \lambda_0 - \kappa \frac{s_r - 1}{t_r}.$$

Nevertheless, with eight parameters ($r=3$) formula (2) does not predict the wave-lengths of the "tails" of the series successfully.

¹ See H. Kayser and C. Runge, *Abhandlungen der kaiserlichen Akademie der Wissenschaften*, Berlin, 1889, Anhang, p. 31.

In the third column of Table V may be found the wave-lengths which the writer has computed from Thiele's own coefficients by

TABLE V

Series	" λ_0 "	"Tail"
α	5165.1733	2768.712
β	5165.5911	2768.712
γ I.....	5163.7023	1759.026
ϵ I.....	5166.2211	2128.362
ϵ II.....	5164.9003	2234.961
δ	5130.5489	2712.408

putting $n = \infty$ in formula (2). Aside from the relatively trivial fact that these wave-lengths are not mutually consistent, the predicted limits fall in a region of the spectrum where no tails have ever been found. In this connection, it is but fair to give the following quotation from Thiele's second paper:¹

Upon the whole it must be evident that these systems of constants are by no means to be considered as definitive and reliable for speculations regarding the true properties of the law of spectral series. The main interest of my computations is not to be found in these constants, but in the tables of computed wave-lengths founded upon them.

SUMMARY

1. The two older methods for calculating the "phase" c of a band series are shown to be too complicated for practical purposes.
2. A new and relatively simple method for evaluating c at different places along a band series is developed.
3. Details of the practical application of the third method are given.
4. The phase is shown to be variable, within specified limits, for the α and δ series of the λ 5165 carbon band, investigated arithmetically by Thiele.
5. The two obvious series starting from the first head of the λ 3883 cyanogen band are shown to be unrelated according to Thiele's scheme of combination.
6. Various lines of evidence are presented to indicate that some of Thiele's hypotheses are invalid.

SLOANE PHYSICAL LABORATORY
YALE UNIVERSITY
May 1915

¹ *Astrophysical Journal*, 8, 12, 1898.

EFFECTIVE WAVE-LENGTHS OF 184 STARS IN THE CLUSTER N.G.C. 1647¹

By EJNAR HERTZSPRUNG

I. THE OBSERVATIONS AND THEIR REDUCTION

The following pages contain the details of my determination of effective wave-lengths in the cluster N.G.C. 1647 ($4^h 40^m, +19^\circ$) briefly described in *Yearbook*, No. 12, p. 222, 1913, of the Carnegie Institution of Washington and referred to by Seares in his paper "The Color of the Faint Stars" in this *Journal* (39, 361, 1914). The instrument employed was the 150-cm (60-inch) Mount Wilson reflector diaphragmed down to 100 cm (40 inches) aperture in order to increase the diameter of the useful field.

Over the end of the tube of the reflector was placed a grating² consisting of overspun rubber cords 3 mm thick separated by free spaces of the same width. This grating forms short spectra on both sides of the central star image as shown in Fig. 1, which is enlarged 3.3 times from the original plate. The focal length of the reflector being 7606 mm (299.5 inches), the distance between the centers of the two spectra of first order is about 1 mm (0.04 inch). When the diameter of the wires of the grating is equal to the spaces separating them, all the spectra of uneven order are at their maximum intensity and all those of even order disappear. In this case the spectra of first order are π^2 times or 2.486 mag. fainter than the star image without grating. As the spectra with the dispersion here used are somewhat elongated, especially for the whiter stars, it will be safer to say that the limiting magnitude down to which, for a certain exposure time, effective wave-lengths can be determined is about 3 mag. less than that for which, under the same conditions without grating, measures of position can be made.³

¹ *Contributions from the Mount Wilson Solar Observatory*, No. 100.

² Made by Toefer of Potsdam.

³ As the spectrum of a red star is sensibly shorter than that of a white one, the loss in light from elongation of the spectra is somewhat smaller for the red than for the white stars. It will therefore be possible to measure the effective wave-lengths of the former down to a magnitude a little fainter than in the case of the latter. It is easy to avoid an undesirable selection caused by this phenomenon by measuring only to a certain intensity of the central image.

Fig. 1 shows the appearance of two stars, of extremely different color. The objects are B.D. $+9^{\circ}4367$, which is a white star, and B.D. $+9^{\circ}4369$, which has a spectrum of the fourth type. The plate received five exposures of 360, 114, 36, 12, and 4 seconds, respectively, so that one step in the exposure time corresponds to 0.5 in its logarithm or to about 1 mag. in intensity. The faintest images are not visible in the figure. A line is drawn between the images of longest exposure for the two stars. The distance is 12.58 mm on the original plate, or $341''.1$ according to the *A.G. Catalogue*. Visually the two stars are of equal brightness—mag-

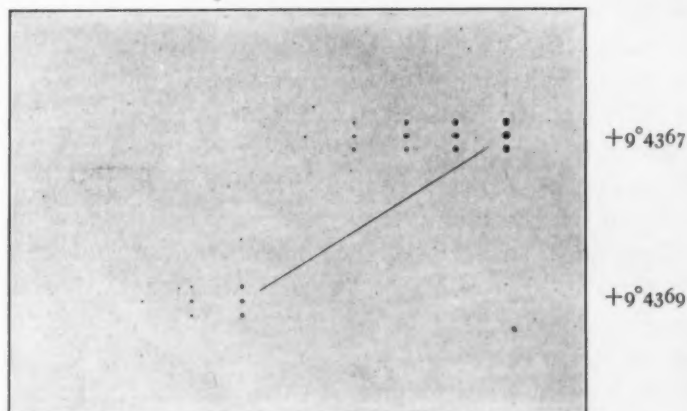


FIG. 1.—Central images and first-order spectra

nitudes 8.5 and 8.7, according to the *B.D.* and magnitudes 8.6 and 8.4, respectively, according to *A.G. Leipzig*. Photographically the difference is about 2 mag. in accordance with the difference in color.

It is seen at a glance, that the distance between the centers of the two spectra of first order is greater for the red ($+9^{\circ}4369$) than for the white ($+9^{\circ}4367$) star, owing to the difference in spectral distribution of energy. This distance between the two spectra determines the effective wave-length and may be taken as an equivalent of color. The mean error of one such distance for well-exposed images is about $\pm 6\mu$, corresponding to $\pm 26\text{ \AA}$ in the effective

wave-length.¹ The effective wave-lengths of the two stars shown in Fig. 1 are found to be 4280 Å for the white star B.D. +9°4367, and 4590 Å for the red star +9°4369, the difference being 310 Å.

The difference in effective wave-lengths for stars of spectra A and K is about 200 Å, while the corresponding difference in color-index, $m_{pg} - m_{vis}$, is 1 mag. The mean error ± 26 Å in one effective wave-length therefore corresponds to a mean error of ± 0.13 mag. in the color-index.

The effective wave-length varies not only with the color of the star but also sensibly with the strength of the spectrum image. To be considered as a color equivalent, therefore, a correction is needed to reduce the measured distance between the two spectra, or the effective wave-length, to a normal intensity of image. This correction will vary with the instrument (reflectors or refractors of different achromatization and focal length), the spectral sensitiveness of the plate, and the color of the star. Its accurate determination requires an undesirable increase of work. I therefore preferred to take several photographs of the same region with different exposures, and on each plate to measure only those spectra which are approximately of normal strength.² Actually the longest exposure given to the plates used in this investigation was 30 minutes, which with 9.5 and 3 minutes, and 57, 18, and 6 seconds, forms a geometrical progression, the logarithm of whose constant ratio is 0.5.

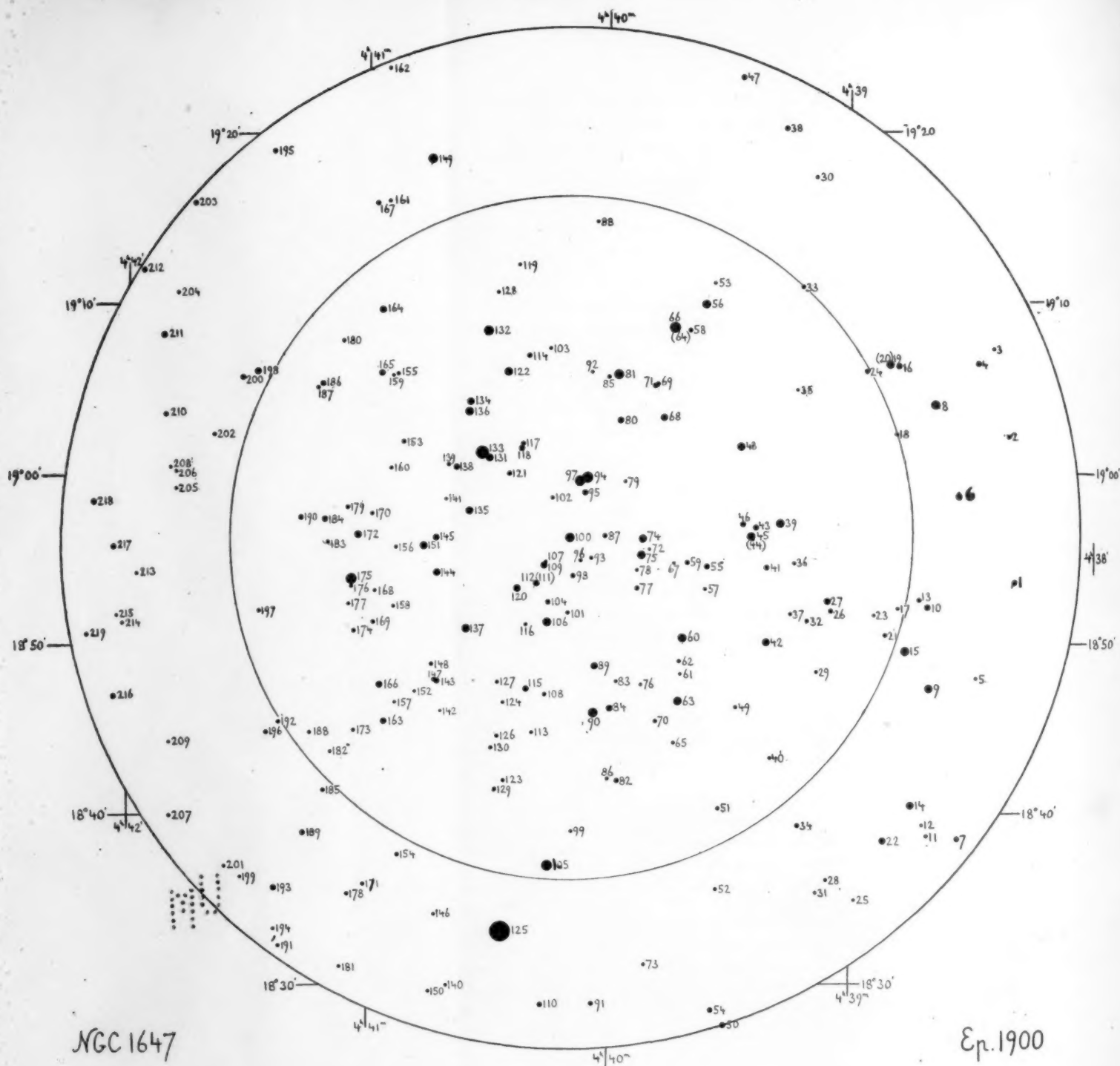
The intensity of images just well exposed was taken as the normal. One effective wave-length from an image of normal intensity was given weight 6; and effective wave-lengths from

¹This accuracy, as is to be expected, is of the same order of magnitude as that attained in the photographic measurement of double stars. With the Copenhagen refractor $a=20$ cm, $f=480$ cm, I found for one exposure, on the average, a mean error of $\pm 4.2 \mu$ for the distance between the two components of a double star. With the 50-cm Potsdam refractor $a=50$ cm, $f=1250$ cm, I found the corresponding mean error to be $\pm 4.5 \mu$.

²From all this it appears that the zero-point of the effective wave-lengths is to a certain extent arbitrary. It would be practicable to define the color-indices and the effective wave-lengths in such a way that the indices 0 mag. and +1 mag. correspond to effective wave-lengths of 4200 and 4400 Å, respectively. To this end 34 Å would have to be subtracted from all the effective wave-lengths given in this and in the following note.



PLATE I



8 9 10 11 12 13 14 15

images 1 and 2 mag. weaker or stronger than the normal intensity received weights 4 and 1, respectively, after the correction for deviation from normal intensity had been applied. No accurate knowledge of the correction to normal intensity is needed, therefore, unless the stars are very bright or very faint. Only for the very faintest stars, which do not reach normal brightness even on the longest-exposed plates, is the correction of any importance.

As an average, I found the effective wave-length to increase 19 Å for each magnitude of increase in the intensity of the image measured. This rate has been adopted for all stars of all colors.¹

A chart of the stars in the cluster N.G.C. 1647, used in this investigation, is given in Plate I. The central star, No. 100, is A.G. Berlin 1290, $4^h40^m9^s.69$, $+18^\circ56'19''.1$ (1900). The diameter of the inner circle is 40' and that of the outer 1°; the central portion being, of course, in much better field than the outer zone, the results derived for the central stars are therefore the most reliable.

TABLE I
LIST OF PLATES

Plate No.	Date	Sid. Time Middle of Exp.	Exp. Time	Kind of Plate
	1912			
249.....	Oct. 13	5^h23^m	30 ^m	Lumière Σ
250.....	"	5 57	30	Seed 27
251.....	"	6 20	9.5	Seed 27
252.....	"	6 33	9.5	Lumière Σ
313.....	16	6 14	30	Lumière Σ
314.....	"	6 53	30	Seed 27
323.....	17	2 15	9.5	Lumière Σ
324.....	"	2 40	30	Seed 27
325.....	"	3 4	9.5	Seed 27
326.....	"	3 27	30	Lumière Σ
327.....	"	4 11	*	Seed 27
328.....	"	4 26	*	Lumière Σ

* 3^m, 3^m, 57^s, 57^s, 18^s, 18^s, 6^s, 6^s.

The plates used are listed in Table I.² As will be seen, there are two complete sets, one taken on Seed "27," the other on

¹ For further details of the method of effective wave-lengths see *Potsdam Publ.*, No. 63, Part 1, 1911. A list of the earlier literature is found in *Astron. Nachr.*, 182, 301, 1909.

² They were measured at the Astronomical Laboratory at Groningen on my return from Mount Wilson to Potsdam.

Lumière "Σ" plates. The two sets have been treated separately. As an average, the effective wave-lengths reduced to the normal strength of image proved to be 29.5 ± 1.5 Å (mean error of median value) greater for the Seed "27" than for the Lumière "Σ" plates. Furthermore, there is a slight indication that this difference between the two sets increases about 2.9 Å for each magnitude of decrease in brightness. The smallness of this magnitude equation is satisfactory.

To reduce the effective wave-lengths to the same system, the Seed "27" plates were first corrected for the constant difference of 29.5 Å between the "Σ" and "27" plates. Secondly, the results from each kind of plate were corrected by half of the magnitude equation, or $\frac{1}{2} \times 2.9$ Å per magnitude. Admitting that this magnitude equation arises only from errors of reduction in the two different sets of plates, the final effective wave-lengths are on the Lumière "Σ" system.

In this system I found from other plates an effective wave-length of 4234 Å to correspond to a typical A star, the color-index of which $I_H = m_{pg} - m_{vis}$, Harvard, is zero according to the *Göttingen Aktinometrie*, B, 1912. It was furthermore found that a difference in the color-index I_H of 1 mag. corresponds to a difference in effective wave-length of 200 Å. Hence we have the following formula for the relation between color-index, I_H , expressed in magnitudes and the effective wave-length λ_{eff} expressed in Å:

$$200 I_H = \lambda_{eff} - 4234.$$

In Table II the reduced effective wave-lengths and their relative weights, as indicated above, are given for each set of plates separately. The weighted means contained in Table IV are the final values.¹

It will be remembered that the weight 6 was assigned to an effective wave-length derived from a single image of normal

¹ Star No. 218, which is 2' inside the border of the field, has accidentally been omitted from this investigation. This mistake is of no importance for the general conclusions. The star is included in the catalogue for the sake of completeness. No. 219 was first called 218. For all other stars my original notation was kept in spite of there being a few objects which proved to be too faint for measurement of effective wave-lengths.

TABLE II
MEAN RESULTS FROM LUMIÈRE "Σ" AND SEED "27" PLATES

STAR No.	LUMIÈRE Σ		SEED 27		STAR No.	LUMIÈRE Σ		SEED 27	
	λ_{eff}	Rel. Wt.	λ_{eff}	Rel. Wt.		λ_{eff}	Rel. Wt.	λ_{eff}	Rel. Wt.
1					51	428	2	431	14
2	4337	10	4358	19	52			597	7
3			372	0	53			384	1
4	334	22	321	30	54	331	14	345	22
5			512	3	55	317	24	336	29
6			421	0	56	389	30	412	29
7	311	17	328	18	57			372	4
8	251	23	269	29	58	333	11	337	22
9	257	28	267	28	59	324	12	347	22
10	287	31	302	29	60	213	28	215	29
11			319	7	61			428	0
12					62	589	3	547	9
13	592	11	570	24	63	250	31	235	30
14	273	30	252	29	64			401	1
15	297	20	298	30	65			512	7
16	337	31	331	31	66	254	29	251	29
17			348	1	67			372	0
18	386	3	348	12	68	333	34	314	32
19	249	32	258	28	69	339	11	332	22
20	324	16	315	19	70	529	3	521	10
21	377	9	368	16	71	318	15	322	25
22	277	33	270	32	72			424	0
23			378	0	73			489	2
24	334	17	321	25	74	265	32	257	30
25			339	0	75	284	32	277	30
26	330	9	342	21	76			347	0
27	302	33	274	29	77	309	12	353	22
28			443	1	78			359	2
29			401	3	79			562	2
30			435	2	80	297	32	298	31
31			497	1	81	249	27	251	30
32	430	3	368	12	82	489	11	482	24
33	315	15	326	25	83			352	2
34	338	15	330	27	84	291	30	290	31
35			559	1	85	352	9	358	17
36			407	4	86			366	3
37			358	7	87	360	10	348	19
38	331	14	335	23	88			361	2
39	241	27	235	29	89	267	37	287	32
40			370	3	90	258	28	252	28
41	354	20	347	26	91	430	7	404	19
42	272	26	271	30	92			322	4
43	300	31	308	30	93			330	7
44			397	1	94	251	30	252	29
45	259	32	254	30	95	304	26	308	28
46	359	22	363	28	96	284	1	347	9
47	328	21	327	30	97	241	29	249	29
48	258	30	261	31	98	323	13	320	24
49	329	3	313	8	99			417	0
50	315	23	308	30	100	282	30	266	29

TABLE II—Continued

STAR NO.	LUMIÈRE Σ		SEED 27		STAR NO.	LUMIÈRE Σ		SEED 27	
	λ_{eff}	Rel. Wt.	λ_{eff}	Rel. Wt.		λ_{eff}	Rel. Wt.	λ_{eff}	Rel. Wt.
101.	288	0	314	7	153.	524	4	501	12
102.	323	0	368	10	154.	391	4	372	14
103.			379	3	155.	516	1	483	9
104.	331	16	330	24	156.			463	1
105.	510	21	515	27	157.				
106.	263	29	268	30	158.			338	3
107.			375	1	159.			392	3
108.	406	3	463	12	160.			321	0
109.	287	32	306	32	161.			432	0
110.	331	10	343	19	162.			370	4
111.	352	4	385	18	163.	278	34	271	32
112.	387	21	391	27	164.	338	32	330	33
113.			388	0	165.	307	31	287	31
114.	332	15	327	24	166.	311	33	297	29
115.	293	28	292	30	167.	334	12	375	22
116.			408	0	168.			360	0
117.	388	10	393	19	169.	357	8	334	16
118.	311	25	306	27	170.	433	0	357	6
119.			484	0	171.	316	0	342	7
120.	371	31	388	31	172.	287	30	287	32
121.	359	10	327	17	173.	351	0	378	6
122.	266	30	270	31	174.	323	6	332	10
123.			353	6	175.	254	25	249	29
124.			333	0	176.				
125.	498	16	512	21	177.			440	1
126.			395	8	178.	305	1	318	9
127.			338	7	179.	421	2	422	9
128.			367	3	180.			355	4
129.			510	0	181.	243	22	235	30
130.			429	0	182.			392	0
131.			326	4	183.	325	5	309	8
132.	280	30	282	30	184.	308	26	303	30
133.	242	31	245	29	185.	307	1	304	8
134.			225	0	186.	326	19	329	26
135.	355	2	347	10	187.	360	5	350	11
136.	344	11	327	19	188.			581	0
137.	266	30	256	30	189.	314	16	317	21
138.	295	29	299	31	190.	228	17	207	25
139.	439	5	462	12	191.			339	4
140.					192.	365	3	357	6
141.					193.	311	31	305	30
142.					194.			368	3
143.	320	25	301	30	195.	341	15	342	24
144.	283	32	297	32	196.	325	8	352	10
145.	315	29	312	30	197.			395	3
146.			483	1	198.	301	32	278	32
147.	298	3	340	9	199.			352	0
148.	346	6	313	11	200.	461	21	468	27
149.	491	23	543	30	201.			464	1
150.			398	1	202.	399	2	418	7
151.	286	32	258	32	203.	551	17	548	25
152.			482	0	204.	382	2	493	7

TABLE II—Continued

STAR NO.	LUMIÈRE Σ		SEED 27		STAR NO.	LUMIÈRE Σ		SEED 27	
	λ_{eff}	Rel. Wt.	λ_{eff}	Rel. Wt.		λ_{eff}	Rel. Wt.	λ_{eff}	Rel. Wt.
205.....					213.....			388	4
206.....			405	4	214.....	299	0	306	7
207.....			374	6	215.....			382	0
208.....			408	0	216.....	306	21	323	28
209.....					217.....	315	22	331	28
210.....	336	15	343	24	218.....				
211.....	558	25	570	31	219.....	339	10	334	12
212.....	306	22	325	28					

intensity, the mean error of such a result being about ± 26 Å. From the differences between the values derived from the Seed "27" and the Lumière " Σ " sets the mean error corresponding to weight 6 is found to be ± 20 Å. The agreement is satisfactory. There is some indication of a systematic error common to all effective wave-lengths derived from the same plate. So far as the material goes, this plate error seems to be of the order of ± 10 Å.

II. DISCUSSION OF RESULTS

Fig. 2 is a graphical representation of the results. The appearance of this diagram is very striking, the most curious fact being the lack of faint white stars. For a further discussion it must be remembered that the effective wave-lengths of the fainter stars, say below magnitude 13, are much less accurate than for the brighter ones. The ordinates of the dotted line in Fig. 2 indicate approximately the value of the mean error of the effective wave-lengths for different magnitudes. The faint stars consequently seem more scattered over the different colors than they really are. Everything taken into consideration, we may say:

The fainter the stars in the region examined, the greater the minimum effective wave-length. This minimum value, which increases with decreasing brightness, is rather sharply defined, and scarcely any stars are to be found with effective wave-lengths less than this limit.

The only faint star which is a pronounced exception to this rule is No. 190 of magnitude 12.40, showing an effective wave-length



of only 4216 Å; the next following of similar magnitude has an effective wave-length of 4316 Å (No. 189), which is 100 Å greater. The star No. 190 is found to be white on 6 plates, so that there can be no doubt about the reality of its exceptional color.

The question arises whether this relation between apparent magnitude and distribution of colors is to be explained by selective extinction of light in space or whether it may be accounted for in other ways. It must be considered that the region in question includes stars belonging physically to the cluster and also other

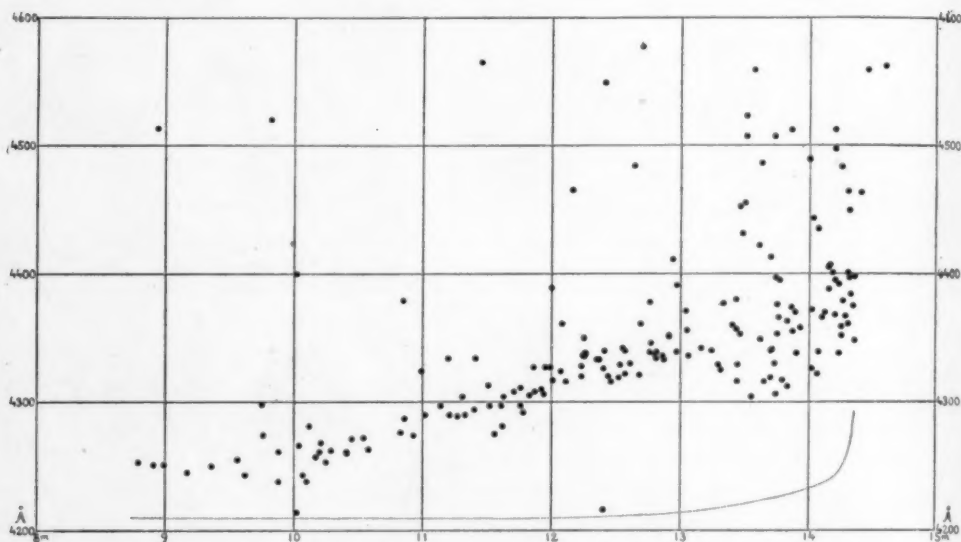


FIG. 2.—Effective wave-lengths and photographic magnitudes in N.G.C. 1647. Dotted curve indicates mean error of effective wave-length.

stars belonging to the system of the Milky Way. The galactic latitude is -15° . All the physical members of the cluster may be considered as at the same distance, and hence for these stars we should expect the relation between color and *apparent* brightness to be about the same as that found for other clusters like the Hyades between color and *absolute* brightness. For the other stars, belonging to the general system of the Milky Way, we may, from all we know, adopt a distribution in space which, in its first approximation, is defined by a rather sharp outer limit beyond which

practically no stars occur. That is to say, stars of a certain apparent brightness cannot have an absolute brightness greater than that corresponding to the limiting distance. The maximum *absolute* brightness must therefore decrease with the *apparent* brightness.

Now for stars of known absolute brightness and color we find that the smaller the absolute brightness, the yellower is the minimum effective wave-length, and that only extraordinary stars occur which are whiter than the limit thus defined.¹ Dividing the stars of N.G.C. 1647 into groups of 29 or 30, I find the following relation between apparent magnitude and the median value of the effective wave-length:

Pg. magnitude	10.02	11.45	12.40	13.06	13.74	14.20	14.45
Eff. wave-length	4260	4300	4327	4347	4364	4389	4396A
O-C	+4	0	-2	-2	-6	+5	+4A

This relation as shown by the differences O-C is well represented by the linear formula:

$$\lambda_{\text{eff}} - 4340 = 30.5 (m - 12.76).$$

The increase in median effective wave-length for each magnitude decrease in apparent photographic magnitude is 30.5 Å. It is remarkable that this rate, all uncertainties taken into consideration, is practically the same as that, namely 26 Å per magnitude, found for stars of known absolute brightness and color within the same interval of effective wave-lengths (4260-4396 Å).² This is what we should expect for stars physically belonging to the cluster. But for the other faint stars we may also expect something similar, for it is a consequence of our ideas of the distribution of stars in space that the median distance of the fainter stars here in question will not vary much with the apparent magnitude.³

¹ See the following article.

² See the following article. The fact that photographic magnitudes have been used here, and visual magnitudes in the following article, has been taken into consideration.

³ The order of magnitude of this median distance of the fainter stars, say of magnitude 14, may be estimated in the following way. For stars of the photographic magnitude 14 we find the median effective wave-length to be 4378 Å. It is obvious

We may therefore say that the results found in this note are in fair agreement with what we know about the distribution of stars in space and the relation between absolute brightness and color. They do not afford any evidence of selective extinction of light in space.

III. DETERMINATION OF THE PHOTOGRAPHIC MAGNITUDES

The photographic magnitudes used in this note have been determined in the following way: During the measurement of the effective wave-lengths, the diameters of the central stars were estimated. Assuming that a difference of 0.5 in the logarithm of the exposure time corresponds to a difference of one magnitude, the estimates were converted into provisional magnitudes. These were used in the manner described above to reduce all the effective wave-lengths measured to the same intensity of image. For the more accurate determination of magnitudes in the central portion of the cluster, the following Schleussner plates were taken on January 14, 1913, by the "Halbgitter" method, with the 80-cm Potsdam refractor:

	Plate No.			
	371	372	373	374
Halbgitter.....	None	None	North	South
Exposure time.....	2×10^m	30^m	30^m	30^m
Sidereal time.....	$3^h 23^m$	$3^h 52^m$	$4^h 59^m$	$5^h 52^m$

The plates were measured with the Hartmann micro-photometer. The zero point of the magnitudes was fixed by

that the "giant" yellow stars will form only a small minority among the yellow stars here considered. Now for "dwarf" stars of known absolute brightness and color the effective wave-length 4378 Å corresponds to an absolute photographic brightness (referred to distance corresponding to $\pi = 1''$) of about +0.5 mag. Assuming the same absolute brightness for the stars of magnitude 14 here considered, we find their median parallax to be 0".002 and their median distance 1600 light-years. This is a plausible value. The parallax of N.G.C. 1647 itself may be estimated in the same way, supposing most of the tenth-magnitude A stars to belong physically to the cluster. Taking the absolute magnitude of these A stars to be -4, we find the parallax to be 0".0016. I imagine that the determination of effective wave-lengths of faint stars will be a valuable help in sounding the Milky Way in different directions. A considerable number of the plates I took at Mount Wilson are meant to serve this purpose.

TABLE III
PHOTOGRAPHIC MAGNITUDES

Star No.	Schleussner "Halb- gitter"	Lumière Σ Estimates	Seed 27 Estimates	Star No.	Schleussner "Halb- gitter"	Lumière Σ Estimates	Seed 27 Estimates
		mag.	mag.			mag.	mag.
1.....			14.45	52.....		13.77	13.70
2.....		12.86	12.95	53.....	14.32		14.30
3.....			14.40	54.....		12.40	12.42
4.....		12.04	11.86	55.....	11.82	11.95	11.92
5.....			14.20	56.....	10.07	9.92	9.94
6.....			14.45	57.....	14.01		14.07
7.....		12.04	12.42	58.....	12.89	12.76	12.85
8.....		9.81	9.94	59.....	12.76	12.67	12.85
9.....		10.31	10.28	60.....	10.04	10.03	9.94
10.....		11.50	11.31	61.....	14.51		14.45
11.....			13.70	62.....	13.55	13.60	13.62
12.....			14.51	63.....	10.06		10.11
13.....		12.76	12.64	64.....			14.30
14.....		10.67	10.50	65.....	13.90	13.77	13.79
15.....		9.68	9.82	66.....	8.83	8.71	8.68
16.....		11.40	11.42	67.....	14.38		14.45
17.....			14.35	68.....	11.00	10.95	11.01
18.....		13.41	13.44	69.....	12.81	12.76	12.85
19.....		10.22	10.28	70.....	13.48	13.60	13.53
20.....	mag.	12.50	12.53	71.....	12.43	12.50	12.42
21.....	13.04	12.95	13.15	72.....	14.57		14.48
22.....		10.95	10.91	73.....			14.00
23.....	14.47		14.51	74.....	10.41	10.40	10.39
24.....	12.39	12.50	12.42	75.....	10.09	10.22	10.17
25.....			14.51	76.....	14.49		14.50
26.....	12.80	12.67	12.75	77.....	12.82	12.76	12.75
27.....	11.32	11.13	11.21	78.....	14.25		14.26
28.....		13.86	14.20	79.....	14.65		14.35
29.....	14.17		14.20	80.....	11.50	11.50	11.62
30.....			14.07	81.....	9.37	9.27	9.41
31.....			14.20	82.....	12.64	12.67	12.64
32.....	13.43	13.41	13.44	83.....	14.23		14.35
33.....	12.62	12.50	12.42	84.....	11.31	11.31	11.42
34.....	12.36	12.58	12.20	85.....	13.10	12.86	13.05
35.....	14.47		14.35	86.....	14.07		14.20
36.....	14.18		14.07	87.....	12.93	12.76	12.95
37.....	14.01	13.77	13.78	88.....			14.30
38.....		12.40	12.31	89.....	10.79	10.95	10.90
39.....	10.16	10.03	9.94	90.....	9.56	9.55	9.55
40.....	14.10		14.20	91.....		13.04	12.85
41.....	12.25	12.22	12.31	92.....	14.15	13.77	14.00
42.....	10.48	10.40	10.39	93.....	13.70	13.77	13.79
43.....	11.66	11.50	11.62	94.....	8.91	8.85	8.95
44.....	14.31		14.30	95.....	11.90	11.95	12.09
45.....	10.18	10.13	10.17	96.....	13.70	13.77	13.70
46.....	12.09	12.13	11.97	97.....	9.13	9.27	9.26
47.....		12.13	11.86	98.....	12.69	12.67	12.64
48.....	10.46	10.31	10.28	99.....	14.40		14.50
49.....	13.80	13.86	13.70	100.....	9.77	9.81	9.69
50.....		11.95	11.58	101.....	13.88	13.77	13.70
51.....	13.46	13.69	13.35	102.....	13.79	13.77	13.62

TABLE III—Continued

Star No.	Schleussner "Halb- gitter"	Lumière Σ Estimates	Seed 27 Estimates	Star No.	Schleussner "Halb- gitter"	Lumière Σ Estimates	Seed 27 Estimates
	mag.	mag.	mag.		mag.	mag.	mag.
103.....	14.27	14.20	155.....	13.64	13.78	13.44
104.....	12.64	12.59	12.53	156.....	14.44	14.35
105.....	8.85	9.02	157.....	14.77	14.39
106.....	10.02	10.13	10.05	158.....	14.24	14.20
107.....	14.36	14.26	159.....	14.24	14.20
108.....	13.43	13.60	13.44	160.....	14.40	14.50
109.....	11.12	11.13	11.21	161.....	14.45
110.....	12.76	12.85	162.....	13.78	14.00
111.....	12.67	12.85	163.....	10.52	10.67	10.60
112.....	11.95	12.04	12.19	164.....	11.22	11.22	11.11
113.....	14.32	14.41	165.....	11.66	11.50	11.51
114.....	12.54	12.50	12.53	166.....	11.29	11.40	11.31
115.....	11.76	11.76	11.86	167.....	12.68	12.69
116.....	14.50	14.41	168.....	14.42	14.45
117.....	13.02	12.76	12.95	169.....	13.22	12.95	13.15
118.....	11.80	11.86	12.19	170.....	13.83	13.78	13.86
119.....	14.56	14.44	171.....	13.69	13.70
120.....	10.83	10.95	10.81	172.....	10.83	10.95	10.90
121.....	13.00	12.77	13.05	173.....	13.73	13.78	13.78
122.....	10.19	10.22	10.28	174.....	13.27	13.23	13.44
123.....	13.74	13.78	175.....	8.92	9.00	9.25
124.....	14.40	14.41	176.....	13.93	14.00
125.....	(6.6)	(6)	177.....	14.31	14.30
126.....	13.78	13.78	13.70	178.....	13.69	13.62
127.....	13.95	13.70	179.....	13.61	13.69	13.54
128.....	14.30	14.20	180.....	13.84	14.00
129.....	14.34	14.45	181.....	9.81	9.94
130.....	14.49	14.50	182.....	14.56	14.50
131.....	14.03	14.00	183.....	13.41	13.32	13.70
132.....	11.61	11.67	11.62	184.....	11.81	11.86	11.86
133.....	9.65	9.55	9.55	185.....	13.50	13.60	13.70
134.....	14.67	14.44	186.....	12.22	12.22	12.31
135.....	13.65	13.60	13.54	187.....	13.48	13.32	13.54
136.....	12.90	12.68	12.95	188.....	14.16	14.41
137.....	10.20	10.31	10.18	189.....	12.38	12.50	12.75
138.....	11.80	11.59	11.75	190.....	12.37	12.50	12.42
139.....	13.54	13.41	13.44	191.....	14.07
140.....	14.55	192.....	13.28	13.60	13.79
141.....	15.3	193.....	11.67	11.75
142.....	15.3	194.....	14.20
143.....	11.95	11.95	11.75	195.....	12.50	12.59
144.....	11.00	11.13	11.00	196.....	13.04	13.44
145.....	11.48	11.50	11.62	197.....	14.20
146.....	14.25	198.....	11.22	11.21
147.....	13.37	13.60	13.54	199.....	14.50
148.....	13.28	13.23	13.54	200.....	12.13	12.19
149.....	9.81	9.82	201.....	14.30
150.....	14.35	202.....	13.69	13.70
151.....	10.49	10.67	10.60	203.....	12.40	12.42
152.....	14.86	14.50	204.....	13.69	13.79
153.....	13.55	13.41	13.44	205.....	14.52
154.....	13.41	13.25	206.....	14.15

TABLE III—Continued

Star No.	Schleussner "Halb- gitter"	Lumière Σ Estimates	Seed 27 Estimates	Star No.	Schleussner "Halb- gitter"	Lumière Σ Estimates	Seed 27 Estimates
		mag.	mag.			mag.	mag.
207.....		13.86	13.86	214.....		13.78	13.70
208.....			14.45	215.....			14.48
209.....			14.55	216.....		12.13	12.09
210.....		12.50	12.64	217.....		12.04	12.09
211.....		10.40	10.50	218.....			
212.....		12.04	11.98	219.....		12.77	13.35
213.....			14.15				

means of plate No. 371, which contained, besides the two exposures of N.G.C. 1647, one of the same duration (10^m) on the central part of the Pleiades.

The extinction constant of the Halbgitter used was not determined directly from photometric measures, but, as described in *Astron. Nachr.*, 199, 247, from the ratio $O-C/C-S_1$, where O is the magnitude of the stellar image without halbgitter, C of the central image behind the halbgitter, and S_1 of the spectra of first order. The constant was thus found to be 2.14 mag. The results are contained in Table III together with the estimates from the diameters of the stars on the Lumière " Σ " and the Seed "27" plates, both reduced to the halbgitter scale. To these three series were assigned the relative weights 4, 1, and 1, respectively. The weighted means are contained in the catalogue, Table IV. The magnitudes of the stars outside the inner field of $40'$ diameter are, of course, very uncertain owing to the neglect of the correction for distance from center of field.

IV. COMPARISON OF EFFECTIVE WAVE-LENGTHS WITH SPECTRA

It will be of special interest to compare the effective wave-lengths found here with the spectra of the same stars. With a mirror of 90 cm (35 inches) focal length, in connection with an objective prism 16×16 cm square, Professor Eberhard has kindly made a few exposures on the cluster, using Seed "30" plates. The best plate was taken on March 1, 1913, from $6^h 0^m$ to $7^h 32^m$ sidereal time, Potsdam. In order to reach stars as faint as possible, the dispersion was very small, the distance between $H\beta$ and $H\epsilon$ being

TABLE IV

CATALOGUE

Star No.	α (1900)*	δ (1900)	Dist. from Center of Field	Ph. Mag.	Effective Wave- Length	Rel. Wt.†
1.....	4 ^h 38 ^m 14 ^s	+18° 53' 5	27'	14.45
2.....	20.	19 2.2	26	12.91	4351	29
3.....	24.	19 7.3	27	14.40	4372	0
4.....	28.	19 6.5	26	11.95	4327	52
5.....	28.	18 48.0	25	14.20	4512	3
6.....	31.	18 58.6	23	14.45	4421	0
7.....	33.	18 38.6	29	12.23	4320	35
8.....	39.	19 4.0	23	9.88	4261	52
9.....	40.	18 47.4	23	10.29	4262	56
10.....	40.	18 52.2	21	11.40	4294	60
11.....	40.	18 38.8	27	13.70	4319	7
12.....	42.	18 39.4	27	14.51
13.....	43.	18 52.6	21	12.70	4577	35
14.....	44.	18 40.3	26	10.58	4263	59
15.....	46.	18 49.6	21	9.75	4298	50
16.....	48.	19 6.3	22	11.41	4334	62
17.....	48.	18 52.1	20.	14.35	4348	1
18.....	48.	19 2.3	20	13.43	4357	15
19.....	50.	19 6.4	21	10.25	4253	60
20.....	50.	19 6.4	21	12.52	4319	35
21.....	51.	18 50.5	19	13.04	4371	25
22.....	51.	18 38.5	26	10.93	4274	65
23.....	54.	18 51.7	18	14.48	4378	0
24.....	56.	19 6.0	20	12.40	4326	42
25.....	58.	18 35.0	27	14.51	4339	0
26.....	39 5	18 52.0	16	12.77	4346	30
27.....	5.	18 52.5	16	11.27	4289	62
28.....	5.	18 36.2	25	14.03	4443	1
29.....	8.	18 48.4	17	14.18	4401	3
30.....	8.	19 17.5	26	14.07	4435	2
31.....	8.	18 35.4	25	14.20	4497	1
32.....	10.	18 51.4	15	13.43	4380	15
33.....	11.	19 11.1	20	12.57	4322	40
34.....	12.	18 39.4	22	12.37	4333	42
35.....	13.	19 5.0	16	14.45	4559	1
36.....	14.	18 54.8	13	14.16	4407	4
37.....	15.	18 51.8	14	13.93	4358	7
38.....	16.	19 20.4	27	12.35	4333	37
39.....	17.	18 57.1	12	10.10	4238	56
40.....	19.	18 43.3	18	14.12	4370	3
41.....	20.	18 54.5	12	12.25	4350	46
42.....	20.	18 50.1	13	10.45	4271	56
43.....	23.	18 56.9	11	11.63	4304	61
44.....	24.	18 56.2	11	14.31	4397	1
45.....	24.	18 56.3	11	10.17	4257	62
46.....	26.	18 57.1	10	12.08	4361	50
47.....	26.	19 23.4	29	11.99	4327	51
48.....	27	19 1.7	11	10.41	4260	61

* The period after the seconds of right ascension indicates an additional 0.5.

† The weight 6 corresponds to a mean error of ± 20 A, and, consequently, weight 1 to ± 50 A, 3 to ± 28 A, 12 to ± 14 A, 24 to ± 10 A, 38 to ± 8 A, 48 to ± 7 A, 67 to ± 6 A.

EFFECTIVE WAVE-LENGTHS OF STARS IN CLUSTER 107

TABLE IV—Continued

Star No.	α (1900)	δ (1900)	Dist. from Center of Field	Ph. Mag.	Effective Wave- Length	Rel. Wt.
49.....	$4^h 39^m 29^s$	$+18^\circ 46'.4$	14'	13.79	4317	11
50.....	31	18 27.7	30	11.76	4311	53
51.....	32	18 40.4	18	13.48	4431	16
52.....	33	18 35.7	22	13.73	4507	7
53.....	33	19 11.3	17	14.32	4384	1
54.....	34	18 28.6	20	12.41	4340	36
55.....	35	18 54.6	8	11.86	4327	53
56.....	37	19 10.1	16	10.02	4400	59
57.....	37	18 53.3	8	14.02	4372	4
58.....	39	19 8.5	14	12.86	4336	33
59.....	40	18 54.9	7	12.76	4339	34
60.....	41	18 50.4	9	10.02	4214	57
61.....	42	18 48.3	10	14.50	4428	0
62.....	42	18 49.1	10	13.57	4559	12
63.....	42	18 46.7	12	10.07	4243	61
64.....	43	19 8.6	14	14.30	4401	1
65.....	43	18 44.2	14	13.86	4512	7
66.....	43	19 8.7	14	8.79	4253	58
67.....	43	18 54.8	6	14.39	4372	0
68.....	46	19 3.4	9	10.99	4324	66
69.....	48	19 5.4	10	12.81	4334	33
70.....	48	18 45.5	12	13.51	4523	13
71.....	48	19 5.3	10	12.44	4320	40
72.....	50	18 55.6	5	14.55	4424	0
73.....	51	18 31.2	25	14.00	4489	2
74.....	51	18 56.1	4	10.41	4261	62
75.....	52	18 55.3	4	10.12	4281	62
76.....	52	18 47.7	10	14.49	4347	0
77.....	52	18 53.3	5	12.80	4337	34
78.....	53	18 54.4	4	14.25	4359	2
79.....	56	18 59.6	5	14.59	4562	2
80.....	57	19 3.2	8	11.52	4297	63
81.....	57	19 5.9	10	9.36	4250	57
82.....	57	18 42.0	15	12.64	4484	35
83.....	58	18 47.9	9	14.25	4352	2
84.....	59	18 46.3	10	11.33	4290	61
85.....	40^o 0	19 5.8	10	13.05	4356	26
86.....	0	18 42.2	14	14.10	4366	3
87.....	1	18 56.4	2	12.91	4352	29
88.....	3	19 14.9	19	14.30	4361	2
89.....	3	18 48.8	8	10.83	4276	69
90.....	3	18 46.0	10	9.56	4255	56
91.....	4	18 29.0	27	12.94	4411	26
92.....	4	19 6.1	10	14.06	4322	4
93.....	4	18 55.1	2	13.73	4330	7
94.....	5	18 59.9	4	8.91	4251	59
95.....	5	18 59.0	3	11.94	4306	54
96.....	7	18 55.0	1	13.71	4341	10
97.....	7	18 59.7	3	9.17	4245	58
98.....	8	18 54.1	2	12.68	4321	37
99.....	9	18 39.1	17	14.42	4417	0
100.....	9	18 56.3	0	9.76	4274	59
101.....	10	18 51.9	4	13.83	4312	7

TABLE IV—Continued

Star No.	α (1900)	δ (1900)	Dist. from Center of Field	Ph. Mag.	Effective Wave- Length	Rel. Wt.
102.....	$4^h40^m14^s$	$+18^\circ58'7''$	3'	13.76	4366	10
103.....	14.	19 7.5	11	14.26	4379	3
104.....	15	18 52.6	4	12.61	4330	40
105.....	15	18 37.1	19	8.94	4313	48
106.....	15	18 51.4	5	10.04	4266	59
107.....	15.	18 54.9	2	14.34	4375	1
108.....	15.	18 47.1	9	13.46	4452	15
109.....	16	18 54.7	2	11.14	4297	64
110.....	16.	18 28.9	27	12.81	4339	29
111.....	17.	18 53.7	3	12.76	4378	22
112.....	18	18 53.7	3	12.00	4389	48
113.....	19	18 44.9	12	14.34	4388	0
114.....	20	19 7.1	11	12.53	4329	39
115.....	20	18 47.5	9	11.78	4292	58
116.....	20.	18 51.2	6	14.48	4408	0
117.....	21	19 1.9	6	12.97	4391	29
118.....	21.	19 1.6	6	11.87	4308	52
119.....	22	19 12.4	16	14.54	4484	0
120.....	22.	18 53.4	4	10.85	4379	62
121.....	24.	19 0.1	5	12.97	4339	27
122.....	25	19 6.1	10	10.21	4268	61
123.....	26	18 42.1	15	13.75	4353	6
124.....	26	18 46.7	10	14.40	4333	0
125.....	26.	18 33.2	23	6.	4506	37
126.....	27.	18 44.7	12	13.77	4395	8
127.....	27.	18 47.9	9	13.90	4338	7
128.....	27.	19 10.8	15	14.28	4367	3
129.....	28	18 41.6	15	14.36	4510	0
130.....	29	18 44.0	13	14.40	4429	0
131.....	29.	19 1.1	7	14.02	4326	4
132.....	30	19 8.5	13	11.62	4281	60
133.....	31.	19 1.4	7	9.62	4243	60
134.....	34.	19 4.4	10	14.62	4225	0
135.....	34.	18 57.9	6	13.62	4349	12
136.....	34.	19 3.7	9	12.87	4333	30
137.....	35.	18 51.0	8	10.20	4261	60
138.....	38	19 0.5	8	11.76	4297	60
139.....	40	19 0.7	8	13.50	4455	17
140.....	40	18 30.1	27	14.55
141.....	40.	18 58.6	8	15.3
142.....	41.	18 46.2	13	15.3
143.....	42.	18 47.9	11	11.92	4310	55
144.....	42.	18 54.3	8	11.02	4290	64
145.....	43	18 56.3	8	11.51	4313	59
146.....	43	18 34.3	23	14.25	4483	1
147.....	43.	18 48.0	11	13.44	4329	12
148.....	44	18 48.9	11	13.31	4325	17
149.....	44.	19 18.7	24	9.82	4520	53
150.....	44.	18 29.7	28	14.35	4398	1
151.....	46	18 55.9	9	10.54	4272	64
152.....	48	18 47.4	13	14.79	4482	0
153.....	51	19 2.0	11	13.51	4507	16
154.....	52	18 37.8	21	13.33	4377	18

EFFECTIVE WAVE-LENGTHS OF STARS IN CLUSTER 109

TABLE IV—Continued

Star No.	α (1900)	δ (1900)	Dist. from Center of Field	Ph. Mag.	Effective Wave- Length	Rel. Wt.
155.....	4 ^h 40 ^m 52 ^s	+10° 6'.0	14'	13.63	4486	10
156.....	53	18 55.8	10	14.40	4463	1
157.....	53	18 46.7	14	14.60
158.....	53.	18 52.3	11	14.23	4338	3
159.....	54	19 5.9	14	14.23	4392	3
160.....	54	19 0.5	11	14.42	4321	0
161.....	54.	19 16.2	23	14.45	4432	0
162.....	55	19 24.1	30	13.89	4370	4
163.....	55.	18 45.6	15	11.56	4275	66
164.....	56.	19 9.8	17	11.20	4334	65
165.....	56.	19 6.1	15	11.61	4297	62
166.....	57	18 47.7	14	11.31	4304	62
167.....	58	19 16.1	23	12.69	4361	34
168.....	58	18 53.3	12	14.43	4360	0
169.....	58.	18 51.4	13	13.16	4342	24
170.....	59	18 57.8	12	13.83	4363	6
171.....	41 1	18 36.0	24	13.70	4340	7
172.....	2.	18 56.5	12	10.86	4287	62
173.....	3	18 45.1	17	13.75	4376	6
174.....	3.	18 50.9	14	13.29	4329	16
175.....	4	18 53.9	13	8.99	4251	54
176.....	4	18 53.5	13	13.94
177.....	4.	18 52.5	14	14.31	4449	1
178.....	5	18 35.4	25	13.65	4316	10
179.....	5	18 58.1	13	13.61	4422	11
180.....	6	19 8.0	18	13.87	4355	4
181.....	7	18 31.2	29	9.88	4238	52
182.....	9	18 43.6	19	14.55	4392	0
183.....	10	18 56.1	14	13.44	4316	13
184.....	11	18 57.4	14	11.83	4305	56
185.....	11	18 41.5	21	13.55	4304	9
186.....	11.	19 5.4	17	12.23	4328	45
187.....	12.	19 5.2	17	13.46	4353	16
188.....	14.	18 44.9	19	14.21	4581	0
189.....	16	18 39.0	23	12.46	4316	37
190.....	17	18 57.6	16	12.40	4216	42
191.....	22	18 32.4	29	14.07	4339	4
192.....	22	18 45.6	20	13.42	4360	9
193.....	23	18 35.8	27	11.71	4308	61
194.....	23	18 33.4	29	14.20	4368	3
195.....	23.	19 19.1	29	12.55	4342	39
196.....	25	18 44.9	21	13.24	4340	18
197.....	27.	18 53.5	18	14.20	4395	3
198.....	28	19 6.2	21	11.21	4290	64
199.....	31.	18 36.5	28	14.50	4352	0
200.....	31.	19 5.8	21	12.16	4465	48
201.....	35.	18 37.1	28	14.30	4464	1
202.....	38.	19 2.4	22	13.70	4413	9
203.....	43.	19 16.1	30	12.41	4549	42
204.....	48.	19 10.8	27	13.74	4397	9
205.....	48.	18 59.3	23	14.52
206.....	48.	19 0.3	24	14.15	4405	4
207.....	49.	18 40.1	29	13.86	4374	6

TABLE IV—Continued

Star No.	α (1900)	δ (1900)	Dist. from Center of Field	Ph. Mag.	Effective Wave- Length	Rel. Wt.
208.....	$4^h 41^m 49^s$	$+19^\circ 0'.5$	24'	14.45	4408	0
209.....	49.	18 44.4	26	14.55
210.....	51.	19 3.7	25	12.57	4340	39
211.....	51.	19 8.3	27	11.45	4565	56
212.....	56.	19 12.2	30	12.01	4317	50
213.....	58	18 54.3	26	14.15	4388	4
214.....	$42^\circ 1'$	18 51.4	27	13.74	4306	7
215.....	3	18 51.8	27	14.48	4382	0
216.....	3.	18 47.1	28	12.11	4316	49
217.....	4	18 55.9	27	12.07	4324	50
218.....	9	18 58.5	28	(11.9)	(4339)
219.....	10	18 50.7	29	13.06	4336	22

only 0.75 mm (0.03 inch). The classification of the spectra could therefore be made only roughly. The results I obtained are given in Table V, arranged according to effective wave-length. The median value of the effective wave-lengths of 23 A-type stars is 4266 Å, which agrees well enough with the value given above for stars of zero color-index, viz., 4234 Å.

TABLE V
EFFECTIVE WAVE-LENGTHS AND SPECTRA

Star No.	Sp.	λ_{eff}	Star No.	Sp.	λ_{eff}	Star No.	Sp.	λ_{eff}
60...	A?	4214	137...	A	4261	198...	A	4290
39...	A	4238	9...	A?	4262	109...	A	4297
181...	F?	4238	14...	A	4263	165...	A	4297
63...	F?	4243	106...	A	4266	15...	F?	4298
133...	A	4243	122...	A	4268	193...	A?	4308
97...	A	4245	42...	A	4271	143...	A?	4310
81...	A	4250	151...	A	4272	68...	A	4324
94...	A?	4251	22...	A	4274	55...	A?	4327
175...	F?	4251	100...	A	4274	164...	F?	4334
19...	A	4253	163...	A?	4275	56...	G, K	4400
66...	A	4253	89...	A?	4276	125...	G, K	4506
90...	A	4255	75...	A?	4281	105...	G, K	4513
45...	A	4257	172...	A	4287	149...	G, K	4520
48...	A	4260	27...	A	4289	211...	G, K, M	4565
8...	A?	4261	84...	A?	4290

POTSDAM

January 25, 1915

EFFECTIVE WAVE-LENGTHS OF ABSOLUTELY FAINT STARS¹

By EJNAR HERTZSPRUNG

It is a well-known fact, of which the stars α and β Orionis may be taken as extreme examples, that absolutely bright stars may have all colors between red and white; but the fainter the absolute brightness, the more limited is the range of color within which the stars are distributed. This limitation is practically one-sided in the sense that only rarely are faint white stars to be found. The less the absolute brightness, the yellower is the color, with only a very few stars which are relatively white.

In order to test this relation between absolute brightness and color down to absolute magnitudes as faint as possible, I took with the 1.5-meter (60-inch) Mount Wilson reflector in the manner described in the preceding article² on N.G.C. 1647 a number of effective wave-length plates of faint stars having large well-known parallaxes. All exposures were made on Lumière " Σ " plates.³ Care was taken to reduce the effective wave-lengths to the same zero-point as those for N.G.C. 1647. The values given here can therefore be directly compared with the former. The effective wave-lengths have been reduced to the same zenith distance.⁴

The results are given in Table I. This table contains among others the absolutely darkest stars so far known, which unlike the companion to Procyon are not too near a bright star for proper examination. The absolute parallaxes are those in *Groningen*

¹ *Contributions from the Mount Wilson Solar Observatory*, No. 101.

² *Mt. Wilson Contr.*, No. 100; *Astrophysical Journal*, 42, 92, 1915.

³ The measures were made at Potsdam, a Toepler machine with measurable movement of plate being used.

⁴ Owing to selective extinction of light in our atmosphere, the effective wave-length of a star increases with its zenith distance. At sea-level this increase amounts to 35 Å in passing from the zenith to a zenith distance of 60°. The greatest difference in corrections occurring here was 26 Å for τ Ceti as compared with stars near the zenith.

TABLE I

Star	α (1900)	δ (1900)	Vis. Mag. Harv.	Abs. μ	Vis. Mag. Red. to $\mu = 1'$	λ eff	No. Images	No. Plates	Sp. η
θ Persei A.	$2^h 37^m 4$	$+48^\circ 48'$	$4^m 23$	$0^s.082$	$-1^m 20$	A	2	1	G
η Cassiop. A.	$0 43.0$	$+57 17$	3.67	$.103$	$+0.10$	4299	3	2	F8
α_2 Eridani A.	$4 10.7$	$-7 40$	4.48	$.179$	$+0.74$	4325	4	2	G5
γ Ceti.	$1 39.4$	$-16 28$	3.65	$.319$	$+1.17$	4415	3	1	K
Mayer 20.	$0 43.1$	$+4 46$	5.82	$.160$	$+1.96$	4462	4	1	K ₂
Σ 443 A.	$3 40.2$	$+41 9$	8.35	$.020$	$(+2.66) $	4393	5	1	G6?
α_1 Cygni A.	$21 2.4$	$+38 15$	5.57	$.298$	$+2.04$	4532	14	2	K8
Σ 443 B.	$3 40.2$	$+41 9$	8.80	$.020$	$(+3.20) $	4527	4	1	G6?
Weisse 17 ^b 322.	$17 20.8$	$+2 14$	7.82	$.126$	$+3.32$	4575	3	1	K9
Σ 1280 A.	$8 46.0$	$+71 11$	8.65	$.099$	$+3.63$	4543	2	1	Ma
Σ 1280 B.	$8 46.0$	$+71 11$	8.65	$.099$	$+3.63$	4533	2	1	Ma
α_1 Cygni B.	$21 2.4$	$+38 15$	6.28	$.208$	$+3.65$	4556	20	2	K8
B.D. +48° 739.	$2 36.1$	$+48 34$	9.62	$.069$	$+3.81$	4440	5	3
η Cassiop. B.	$0 43.0$	$+57 17$	7.41	$.103$	$+3.84$	4512	7	2
Σ 1321 A.	$9 7.6$	$+53 7$	8.0	$.155$	$+3.95$	4533	4	1	K8
Σ 1321 B.	$9 7.6$	$+53 7$	8.0	$.155$	$+3.95$	4533	4	1	K8
O Σ 547 A.	$0 0.3$	$+45 16$	9.31	$.105$	$+4.42$	4404	4	1	K5
O Σ 547 B.	$0 0.3$	$+45 16$	9.31	$.105$	$+4.42$	4534	4	1
θ Persei B.	$2 37.4$	$+48 48$	9.86	$.082$	$+4.43$	4504	4	1
Groom. 34 A.	$0 12.5$	$+43 27$	7.97	$.281$	$+5.21$	4520	12	2	Ma
Lal. 46650.	$23 44.0$	$+1 52$	9.09	$.182$	$+5.39$	4408	6	3	Ma
O Σ 547 C.	$0 0.3$	$+45 16$	10.51	$.105$	$+5.62$	4498	4	2
Lal. 21185.	$10 57.9$	$+30 38$	7.60	$.410$	$+5.66$	4512	9	1	Ma
α_2 Eridani BC.	$4 10.7$	$-7 40$	9.48	$.179$	$+5.74$	4179	6	1	AO
AOe 17415-6.	$17 37.0$	$+08 20$	9.1	$.268$	$+6.24$	4505	5	3	Mb
Krüger 60 A.	$22 24.4$	$+57 12$	9.59	$0^s.256$	$+6.63$	4531	7	6	Mb

	$18^h 41^m 8$	$+59^{\circ} 29'$	$9^m 33$	$\sigma^s 293$		A	I3		Ma
$\Sigma 2398$ A.....	18 41.8	$+59^{\circ} 29'$	9.33	.293	$+6^m 66$	4520	13	4	K
$\Sigma 2398$ B.....	18 41.8	$+59^{\circ} 29'$	10.10	.293	$+7^m 43$	4530	9	5	F
Groom. 34 B.....	0 12.5	$+43^{\circ} 27'$	10.99	.281	$+8^m 33$	4574	4	4
Krüger 60 B.....	22 24.4	$+57^{\circ} 12'$	11.59	.256	$+8^m 63$	4544	5	4
2 yellow Hyades,* mean.....	3.08	.025	$-4^m 04$	4442	3	3	K
8 white Hyades,† mean.....	5.81	.025	$-2^m 21$	4301	18	5	F
5 satellites of Saturn,‡ mean.....	$[-0^m 33]$	4368	10	5
Planetoid (8) Flora.....	$[-0^m 33]$	4408	4	1
Color-indices transformed into effective wave-lengths:									
Helium stars, general mean.....	$-8^m 58$	[4188]	A
8 stars of the Ursa Major group §, mean.....	$-4^m 38$	[4237]
α Lyrae.....	18 33.6	$+38^{\circ} 41'$	0.14	.097	$-4^m 93$	[4234]	A0
β Cassiop.....	0 3.8	$+58^{\circ} 36'$	2.42	.073	$-3^m 26$	[4318]	F5
α Aquilae.....	19 45.0	$+8^{\circ} 6'$	0.89	.203	$-2^m 57$	[4280]	A5
γ Virg. A or B.....	12 36.6	$-0^{\circ} 54'$	3.66	.071	$-2^m 08$	[4282]	F
ζ Herculis.....	16 37.5	$+31^{\circ} 47'$	3.00	.101	$-1^m 98$	[4337]	Go
α Canis Min.....	7 34.1	$+5^{\circ} 29'$	0.48	0.324	$-1^m 97$	[4308]	F5

* B.D. $+15^h 53^m 11$ and $+17^h 71^m 12$.

† B.D. $+15^h 62^m 1$, 625, 633, 636, 637, 639, 640, and 645.

‡ Tethys, Dione, Rhea, Titan, Japetus.

§ β , γ , δ , ϵ , and ζ Ursa Maj., α Coron. Bor., β Aurigae, α Canis Maj.

|| The components of the double star $\Sigma 443$ have been omitted from Fig. 1 on account of the great relative uncertainty of their parallax.

¶ I am indebted to Mr. W. S. Adams for some unpublished data.

Publications, No. 24, due regard having been given to additional measures.

Judging from the common proper motion and radial velocity, the brighter stars belonging physically to the system of the Hyades are, as is well known,¹ divided into two distinct groups, one consisting of a few yellow stars and the other of white stars, which form the majority. The mean effective wave-lengths for two yellow and for eight white physical members of the Hyades have been entered in the table.

Concerning our sun, I have been able to determine the effective wave-length of its light only as reflected by five of the satellites of Saturn and by the planetoid (8) Flora.² The weighted mean (5 to 1 according to the number of objects), 4375 Å, has been entered in the diagram (☉) on the assumption that the quality of the sun's light is not seriously altered by the reflections in question.³ Finally, for a few bright stars of well-known parallax, I have transformed the color-indices, *I*, given by E. S. King,⁴ into effective wave-lengths by the formula

$$\lambda_{\text{eff}} = 4234 + 210 I.$$

These results are to be found in brackets in Table I.

All the results are shown graphically in Fig. 1. The full line represents the radiation of a black body of the size of our sun. The points represent the stars, and the sign ☉, the reflected sunlight, for which the effective wave-lengths have been determined. The circles show the color-indices by King, transformed into effective wave-lengths.

The appearance of this diagram is interesting. When we neglect the absolutely bright yellow stars, which are represented in the figure by the mean of only two bright yellow Hyades, we may state the following:

¹ Cf. *Potsdam Publ.*, No. 63, p. 26, 1911.

² October 16, 1912, 23^h3 sidereal time. Three underexposed plates of (433) Eros were obtained on September 11, 1912, between 20^h5 and 21^h4 sidereal time. The uncertain effective wave-length derived is 4506 Å.

³ It may be recalled that the satellite I of Jupiter (Io) shows a markedly greater effective wave-length than satellites II, III, and IV (*Potsdam Publ.*, No. 63, p. 40).

⁴ *Harvard Annals*, 59, 177, 1912.

On the supposition that stellar surfaces radiate approximately as a black body, the relation between absolute brightness and color from absolute magnitude -7 to $+3$ deviates from the same relation for a black body (full line) in the same way, and approximately to the same extent, as we should expect from the known increase in density¹ and decrease in mass² with decreasing absolute brightness. But below absolute brightness $+3$ mag., between $+3$ and

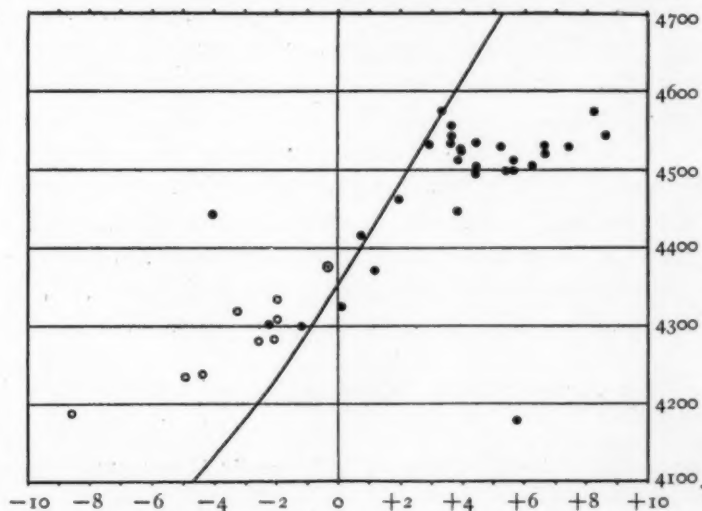


FIG. 1.—Abscissa: Absolute magnitude (sun = -0.33)
Ordinate: Effective wave-length

$+8$ mag., the deviation from the radiation of a black body is too great to be explained by facts already known.

With the single exception of the white faint companion to α_2 Eridani³ we may say that the stars between absolute magnitudes

¹ Shapley, *Astrophysical Journal*, **38**, 158, 1913. The average density of a star of the first spectral type may be taken to be about 0.1 of that of our sun.

² The statistics of spectroscopic binaries have been specially investigated by H. Ludendorff, *Astron. Nachr.*, **189**, 145, 1911.

For 15 stars with known mass and parallax I find a decrease of 0.06 ± 0.01 (mean error) in the logarithm of the mass for each magnitude of decrease in absolute brightness.

³ This exception is, in fact, very strange. It is the well-known double star Σ 518, which has a proper motion of $4''.1$ yearly in common with α_2 Eridani. The combined magnitude of the two components is 9.48 mag. and the difference about 1.7

+3 and +8 are approximately all of the same color.¹ Proceeding from the absolutely brightest stars to the fainter ones, evidently a new unknown element comes into action at about absolute brightness +3, which stops the further increase in effective wave-length with decreasing absolute magnitude.²

If the difference of 5 mag. in the absolute brightness between +3 and +8 mags., within which the color remains constant, were due only to differences in the size of the stars, the ratio of mass to density would be 1000 times greater at absolute magnitude +3 than at +8. We cannot imagine such a difference as due to change in density alone.

Concerning the mass, we are able to eliminate the effect of its variation on the size of a star when the object is one of the components of a double star the apparent orbit of which, together with the ratio of the masses of the two components, is known. Call the masses of the two components, in terms of the sun, M_1 and M_2 ; their apparent magnitudes, m_1 and m_2 ; the apparent major axis

mag. From the apparent orbit and the parallax, which are both approximately known, we find the sum of the masses to be $M_1 + M_2 = 0.76 \odot$. This is no exceptional value.

At the Solar Union, 1913, Professor H. N. Russell told me that this star had been found at Harvard to have a spectrum of Class A. This agrees with Adams, who found the spectrum to be A (*Publ. Astron. Soc. Pacific*, 26, 198, 1914), and with my effective wave-length.

The exceptionally white color of the faint companion to α_2 Eridani recalls the white 12.4 mag. star No. 190 of the cluster N.G.C. 1647 (compare the preceding article). Perhaps there is also physical analogy between these two stars.

In this connection it may be noted that Adams has found the 7.3 mag. star Lal. 28607 ($15^h 37^m 7$, $-10^\circ 37'$; 1900), the proper motion of which is $1''.17$ yearly, to have an A spectrum and a radial velocity of -170 km. The absolute brightness of this star, when estimated from these data in the way described in *Astron. Nachr.*, 185, 92, 1910, is found to be -1.3 ± 2.45 mag. (mean error). The absolute brightness may therefore very well be the normal value for an A star, namely, about -4 mag. The measured parallax, $+0''.03$, is very uncertain.

¹ From different sides it has been suggested to me that this phenomenon might be due to the rapid falling-off of the sensibility of the plate at the end of longer wave-lengths of spectrum. In objection to this I wish to mention that the linear relation between color-index and effective wave-length still holds for fourth-type stars with a color-index of about +2 mag. and an effective wave-length of about 4600 Å.

² The earlier inferior results, *Potsdam Publ.*, No. 63, p. 40, 1911, showed only the general increase of effective wave-length with decreasing absolute brightness.

of the orbit in seconds of arc, a ; and the period in years, P . The absolute magnitude (for a parallax $\pi=1''$) of a star having the same surface brightness and density as, for instance, the first component, and the same mass as the sun, will then be:

$$m_1, \pi=1'', M=\odot = m_1 + \frac{5}{3} \log \frac{a^3}{P^2 \left(1 - \frac{M_2}{M_1}\right)}.$$

The number of double stars of known mass ratio being small, I have adopted for other double stars equality of masses. Especially when the two components are nearly equal in brightness and color is this assumption plausible.

We may still increase the number of objects reasonably well suited to this investigation by including double stars when only the first trace of orbital motion has been observed. For such double stars we are able to calculate a minimum value¹ of a^3/P^2 . Mr. C. Luplau-Janssen has kindly examined statistically all double stars with known orbits and found that the true value of a^3/P^2 is on the average $(1.65)^3$ times greater than the minimum value derived from a single element of the apparent orbit.²

By these more or less tentative methods the values given in Table II and shown in Fig. 2 were found. It will be admitted that the effect of differences in mass on the size of the stars has been eliminated to a great extent; nevertheless, Fig. 2 has the same general appearance as Fig. 1. We may therefore conclude that differences in mass are as little capable as differences in density of explaining the constancy of color between the absolute magnitudes +3 and +8.

It is an obvious suggestion for the explanation of the fact found above that the absolute magnitude +3, corresponding to the temperature 3400° Abs. of a black body of the size of the sun, represents the stage of a cooling star at which the formation of relatively dark solid matter on its surface begins, the remaining

¹ *Astron. Nachr.*, 190, 113, 1911.

² The proportion between the true value of $aP-\frac{1}{2}$ and its minimum value does not vary much for different double stars. The mean deviation from the logarithm of the mean ($\log 1.65=0.22$) is about ± 0.085 , corresponding to ± 0.43 mag.

fluid part giving practically all the radiation. At any rate, these absolutely dark stars deserve further attention. They should, for one thing, be examined for variability in light.

It must be kept in mind that the longer effective wave-lengths especially depend only upon the distribution of energy within a

TABLE II

Star	Vis. Mag. Harv.	Minimum Hypo- thetical π $M_1 + M_2 = \odot$	Hypo- thetical π $M_1 + M_2 = \odot$	M_2/M_1	Hypo- thetical Abs. Mag.	λ_{eff}
						A
ζ Orionis A.....	2 ^m 05	0 ^s .008	1	-7 ^m 85	[4154]
γ Leonis A.....	2.61	.024	1	-4.90	[4442]
ζ Urs. Maj. A.....	2.40	.027	1	-4.86	[4240]
β Aurigae A.....	2.82	0 ^s .040	1	-4.66	[4219]
α Urs. Maj. A.....	1.95	.040 ^s	1	-4.43	[4474]
α Gemin. A.....	1.99117	1	-3.17	[4257]
α Can. Maj. A.....	-1.58568	0.39	-3.05	[4272]
δ Gemin. A.....	3.53	.038	1	-2.99	[4314]
ϵ Urs. Maj. A.....	3.12	.061 ^s	1	-2.35	[4297]
α Can. Min. A.....	0.48352	0.33	-1.90	[4308]
ζ Herculis A.....	3.05128	0.43	-1.67	[4337]
γ Virginis A.....	3.65119	1	-1.47	[4282]
θ Persei A.....	4.23	.067	1	-1.05	4299
Sun.....	-26.9	-0.33	(4375)
η Cassiop. A.....	3.67200	0.76	-0.23	4325
Σ 443 A.....	8.35	.024	1	+0.84	4393
Σ 443 B.....	8.89	.024	1	+1.38	4527
Σ 1280 A.....	8.65	.048	1	+2.64	4543
Σ 1280 B.....	8.65	.048	1	+2.64	4533
61 Cygni A.....	5.57	.199	1	+2.65	4532
η Cassiop. B.....	7.41200	0.76	+3.31	4512
61 Cygni B.....	6.28	.199	1	+3.36	4556
O Σ 547 A.....	9.31	.059	1	+3.75	4494
O Σ 547 B.....	9.31	.059	1	+3.75	4534
Σ 1321 A.....	8.0	.120	1	+3.98	4523
Σ 1321 B.....	8.0	.120	1	+3.98	4523
Groom. 34 A.....	7.97	.123	1	+4.00	4529
θ Persei B.....	9.86	.067	1	+4.58	4504
α_2 Eridani B.....	9.69	0.163	1	+5.25	4179
Σ 2398 A.....	9.33	.123	1	+5.36	4520
Krüger 60 A.....	9.59	.134	1	+5.81	4531
Σ 2398 B.....	10.10	.123	1	+6.13	4530
Groom. 34 B.....	10.99	.123	1	+7.02	4574
Krüger 60 B.....	11.59	0.134	1	+7.81	4544

narrow part of the spectrum. It would be of special interest to have the results found here confirmed by measuring the color-indices.

As all my plates were taken between July 18 and October 17, 1912, inclusive, a number of faint stars with well-known parallaxes could not be included in this note.

I am greatly indebted to the director of the Mount Wilson Solar Observatory, Professor George E. Hale, who not only immediately granted my request to use the 60-inch reflector for the determination of effective wave-lengths, but also offered his assistance in realizing my plans. I owe the main part of the necessary funds

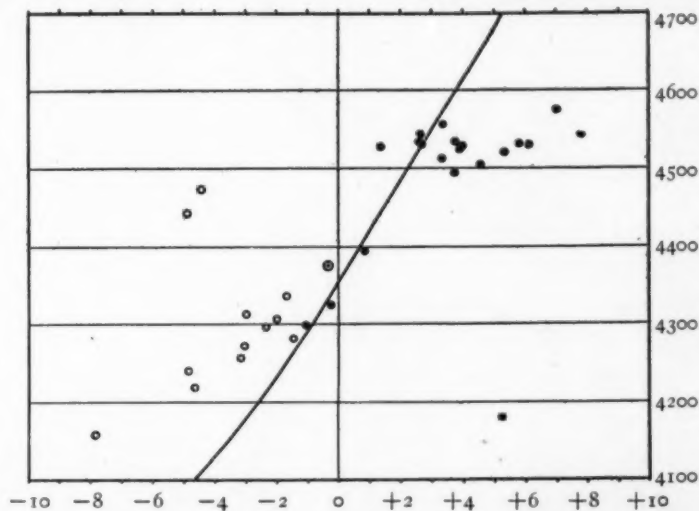


FIG. 2.—Abscissa: Hypothetical absolute magnitude (mass = \odot)
Ordinate: Effective wave-length

and five months' leave from Potsdam to the Prussian government and the Academy of Science of Berlin. I wish also to express here my best thanks for the kind and disinterested help given to me by all of the Mount Wilson Observatory staff, not the least to Mr. Hoge, the indefatigable night assistant.

POTSDAM ASTROPHYSICAL OBSERVATORY
January 25, 1915

COLOR-INDICES IN THE CLUSTER N.G.C. 1647¹

By FREDERICK H. SEARES

I. INTRODUCTION

For the determination of the color of the stars two methods are available. The first, with the aid of a coarse objective grating, measures directly the mean effective wave-length of the light which impresses itself upon the photographic plate,² while the second compares the relative intensities of the radiation in two more or less widely separated regions of the spectrum. The latter method is most conveniently applied by choosing for the comparison the spectral regions whose intensities are expressed by the photographic and the visual, or photo-visual, magnitudes. The measure of the color is then

$$\text{Color-index} = C = Pg - Pv,$$

in which Pg and Pv are the photographic and photo-visual magnitudes of the star in question.

With suitable instrumental equipment the measurement of the effective wave-length is an expeditious and convenient method of procedure; but since precise magnitudes are required for the investigation of many questions, the determination of star colors is readily made incidental to the measurement of brightness, so that the second method also has its advantages.

The mutual control afforded by two processes so different in their observational details is invaluable, especially as both are liable to more or less troublesome systematic errors. The effective wave-length, for example, depends upon the intensity of the small spectral image from which it is derived, and the results must accordingly be reduced to a normal intensity. Hertzsprung avoids the greater part of the difficulty by making a number of exposures on the same plate with gradually increasing exposure time, and

¹ *Contributions from the Mount Wilson Solar Observatory*, No. 102.

² Hertzsprung, *Potsdam Publ.*, 22, No. 63, 1911. The earlier literature is listed in *Astron. Nachr.*, 182, 301, 1909.

then selecting for measurement only those images which, as nearly as possible, are of a certain standard intensity. The color-index, on the other hand, shown by the equation defining it, is seriously influenced by relative errors in either the slope or the zero-point of the magnitude-scales.

As the precise determination of a scale of magnitudes is not an easy matter, the color-index is peculiarly liable to error, and the difficulty increases rapidly with decreasing brightness of the stars. To be useful, color results must be homogeneous; they must be directly comparable, whatever the relative brightness of the stars to which they refer. It is not sufficient, therefore, that the magnitudes should be relatively accurate for a limited range; in both scales and for all degrees of brightness, they must be correct relatively to the zero-point defined by the stars of the sixth magnitude. If either scale is in error, the equation

$$C = P_g - P_v$$

will give an incorrect result unless the other happens also to be in error by the same amount. The demand is therefore exacting, especially when it becomes a question of the color of the fainter stars, for with these the cumulative error in the scales has its greatest effect.

In fact, the difficulties hitherto experienced in establishing satisfactory scales of magnitude have been so considerable that it is advantageous to utilize in another direction the possibilities of the two methods of color determination by employing them to test the reliability of the scales. Given a series of carefully determined effective wave-lengths, we can, by means of stars of known color-index, turn the entire series into color-indices. A comparison with the corresponding results obtained directly from the magnitudes will then show at once the relative errors of the scales, although not their absolute values. Any systematic error in the effective wave-length is of course also involved; but this is small, and probably but little dependent upon the brightness of the objects observed, while the uncertainty affecting the color-indices derived from the magnitudes of faint stars is relatively large. It is not to be understood that the errors inherent in the colors derived from

magnitudes are necessarily large, for when once we have been assured that reliable magnitudes are available, it is probable that the two methods will give results comparable in precision. The difficulty is that we have no such assurance—in fact, no independent control which is capable of specifying what the uncertainties affecting the magnitude-scales may be.

II. OBSERVATIONS

It is the purpose of this note to test in the manner indicated the photographic and photo-visual scales established at Mount Wilson for stars near the North Pole. Effective wave-lengths for these objects are not available, but Hertzsprung has derived such results for nearly 200 stars in another region, N.G.C. 1647, which are immediately applicable to the problem.¹ To effect a comparison it is only necessary to transfer the polar scales to the region of the cluster by photographs of multiple exposure.

To this end comparisons were made between the Pole and the cluster, using the same kinds of plates as in the investigation of the polar magnitudes—Seed “27” for photographic, and Cramer “Inst. Iso.” with a yellow filter for photo-visual magnitudes. Five separate transfers of each scale were made, and to minimize atmospheric irregularities no two of the same kind were undertaken on the same night.² In all cases the exposures were symmetrically arranged, usually in the order: cluster, Pole, Pole, cluster; the exposure times were short, 2^m for Seed “27,” and 5^m for “Iso.” plates.

The photographs were measured and corrected for distance error in the usual way. The magnitudes of the stars in the cluster were read from curves derived from the scale-readings and the magnitudes of the Mount Wilson Polar Standards.³ After correction for extinction the results were combined into the mean values which appear in the second and third columns of Table II. Owing to temperature fluctuations of unusual magnitude, the largest images

¹ *Mt. Wilson Contr.*, No. 100; *Astrophysical Journal*, 42, 92, 1915.

² I am indebted to Mr. P. J. Van Rhyse for one of the pairs of polar comparison plates here used.

³ *Mt. Wilson Contr.*, No. 97; *Astrophysical Journal*, 41, 206, 1915.

on some of the plates were unsuitable for measurement. As these have been excluded, the objects listed begin at about magnitude 11.5; the faintest shown is 15.45. The plates were centered on star No. 100 of Hertzprung's list and, within the limits of the useful

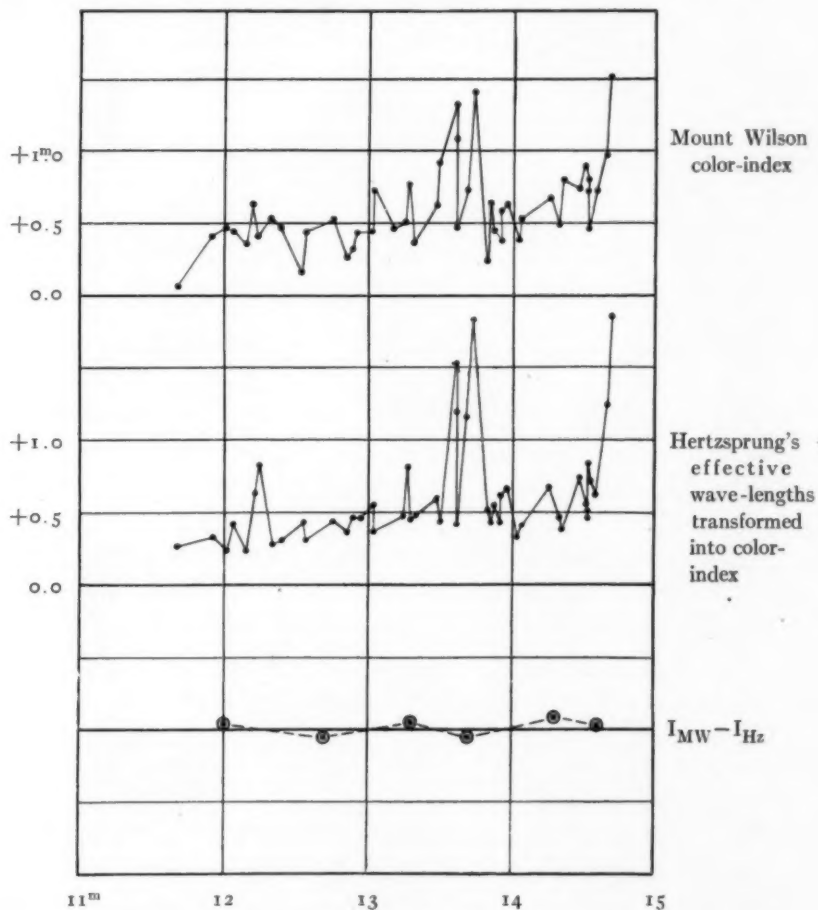


FIG. 1.—Color-indices and photographic magnitudes

field which is 23' in diameter, there are nearly fifty stars available for comparison with his effective wave-lengths.

As there is but little information bearing upon the precision with which polar comparisons can be effected, Table I may be of interest.

It shows the divergence of the results of individual polar comparison plates from the mean scales for the cluster. The unit is 0.01 mag. and the quantities in parentheses indicate the number of stars used in deriving each mean residual. The zero-point residuals relative to the mean zero-point established by all plates of the same kind are shown in the second line at the bottom of each

TABLE I
SCALE DIVERGENCE FOR MAGNITUDES IN N.G.C. 1647

MEAN MAG.	PHOTOGRAPHIC PLATES				
	1392	1405	1417	1428	VR1
12.1.....	+11 (8)	-6 (5)	+12 (8)	-12 (8)	- 8 (7)
12.7.....	+ 3 (5)	+4 (6)	+15 (5)	- 8 (6)	-11 (6)
13.3.....	+ 7 (7)	-9 (7)	+ 2 (7)	- 3 (7)	+ 2 (7)
13.7.....	+ 2 (9)	+5 (9)	- 4 (9)	+ 1 (9)	- 4 (9)
14.3.....	- 1 (6)	+4 (6)	- 5 (6)	+ 6 (6)	- 3 (6)
14.6.....	- 4 (8)	-1 (8)	0 (8)	+ 2 (8)	+ 4 (7)
14.9.....	- 7 (8)	-2 (8)	-10 (8)	+ 3 (8)	+16 (8)
A.D.....	9.5	9.3	11.5	10.0	14.2
Z.P.....	-6.2	+0.1	+14.3	-11.1	+ 2.8
No.....	51	49	51	52	50
MEAN MAG.	PHOTO-VISUAL PLATES				
	1393	1406	1418	1429	VR2
12.1.....	- 3 (8)	-2 (8)	+ 4 (8)	+ 7 (8)	- 6 (7)
12.7.....	-10 (6)	-5 (6)	+ 4 (6)	+12 (6)	- 1 (6)
13.3.....	+12 (5)	-4 (7)	- 6 (7)	+10 (7)	- 8 (7)
13.7.....	+ 9 (3)	+5 (7)	- 5 (9)	- 7 (9)	+ 5 (9)
14.3.....	+5 (5)	+ 3 (5)	-13 (6)	+ 7 (6)
14.6.....	0 (2)	+16 (3)	- 9 (6)	+ 4 (6)
A.D.....	10.5	7.3	8.2	11.3	11.0
Z.P.....	-11.0	-1.5	+9.4	+ 7.2	- 3.6
No.....	22	35	38	42	41

section of the table. The average deviation of a single magnitude and the total number of stars also appear at the bottom of each section. The probable error of a single determination of the zero-point is ± 0.06 mag., and of the mean from five plates ± 0.025 mag. The probable value of the constant error in the color-indices arising from the transfer of the scales is therefore ± 0.035 mag.

Table II contains the detailed results for individual stars. The numbers in the first column are those of Hertzsprung; the co-ordinates may be found by consulting his list.¹ The derivation of the Mount Wilson photographic and photo-visual magnitudes in the second and third columns has already been described. The number of values upon which each is based appears in the fifth column. In the fourth and sixth columns, respectively, are the Mount Wilson color-index and its weight. Then follow Hertzsprung's effective wave-length and its weight, the color-index obtained from λ_e , the difference between the two color-indices and its weight, and finally, as a check upon the scales, a comparison of the Mount Wilson photographic magnitudes with those of Hertzsprung.

III. TRANSFORMATION OF EFFECTIVE WAVE-LENGTHS INTO COLOR-INDICES

The data for the comparison of the effective wave-lengths with the color-indices were very kindly supplied in manuscript by Professor Hertzsprung some months before his paper was received for publication, and in consequence some of my results differ slightly from his. Allowance, however, is easily made for these differences.

The data bearing on the relation between λ_e and C here used are as follows: From 15 white stars, mean C (Harvard) = +0.21 mag., distance between first-order spectra is

$$D = 1.0780 \pm 0.0026 \text{ mm.}$$

From 11 red stars, mean C (Harvard) = +1.22 mag.,

$$D = 1.1338 \pm 0.0030 \text{ mm.}$$

$\Delta C = +1.01$ mag. is equivalent to

$$\Delta D = 0.0558 \pm 0.0040 \text{ mm or } \Delta \lambda = 222 \pm 16 \text{ \AA.}$$

From these and other data Hertzsprung adopts an increase of 200 \AA in λ_e as the equivalent of a change of 1 mag. in the Harvard color-index. We have, however, the following relations between the Harvard and Mount Wilson color-indices:

$$\begin{aligned} +0.21 \text{ Harvard} &= +0.21 \text{ MW} \\ +1.22 \text{ Harvard} &= +1.45 \text{ MW.} \end{aligned}$$

¹ *Mt. Wilson Contr.*, No. 100; *Astrophysical Journal*, 42, 97, 1915.

TABLE II
MAGNITUDES, EFFECTIVE WAVE-LENGTHS, AND COLOR-INDICES

No.	MOUNT WILSON					HERTZSPRUNG			C_W minus CHz	WT. OF DIFF.	P_{8W} minus P_{8Hz}
	P_g	P_v	C_W	n	Wt. C	λ_e	Wt. A	CHz			
43...	11.69	11.62	+0.07	3, 4	17	4304	61	+0.27	-0.20	13	+6
44...	14.53	13.80	+0.73	4, 2	12	397	1	+0.85	-0.12	1	+22
46...	12.21	11.57	+0.64	4, 5	22	361	50	+0.63	+0.01	15	+13
55...	12.08	11.64	+0.44	4, 5	22	327	53	+0.42	+0.02	16	+22
57...	14.27	13.58	+0.69	5, 4	22	372	4	+0.69	0.00	3	+25
59...	12.90	12.59	+0.31	5, 5	25	339	34	+0.48	-0.17	14	+14
61...	14.78	13.75	+1.03	5, 1	8	428	0	+1.04	-0.01	0	+28
62...	13.74	12.33	+1.41	5, 5	25	559	12	+1.84	-0.43	8	+17
67...	14.67	13.90	+0.77	5, 2	14	372	0	+0.69	+0.08	0	+28
69...	13.50	12.58	+0.92	5, 5	25	334	33	+0.45	+0.47	14	+69
71...	13.04	12.31	+0.73	5, 5	25	320	40	+0.38	+0.35	15	+60
72...	14.96	14.11	+0.85	5, 2	14	424	0	+1.01	-0.16	0	+41
76...	14.91	13.81	+1.10	5, 1	8	347	0	+0.54	+0.56	0	+42
77...	12.92	12.48	+0.44	5, 5	25	337	34	+0.48	-0.04	14	+12
78...	14.53	13.80	+0.73	5, 2	14	359	2	+0.61	+0.12	2	+28
79...	14.70	13.16	+1.54	5, 4	22	562	2	+1.86	-0.32	2	+11
80...	12.01	11.53	+0.48	5, 5	25	297	63	+0.23	+0.25	18	+49
83...	14.51	13.61	+0.90	5, 1	8	352	2	+0.57	+0.33	2	+26
85...	13.49	12.87	+0.62	5, 4	22	356	26	+0.60	+0.02	12	+44
87...	13.03	12.58	+0.45	5, 5	25	352	29	+0.57	-0.12	13	+12
92...	14.36	13.56	+0.80	5, 4	22	322	4	+0.39	+0.41	3	+30
93...	13.92	13.54	+0.38	5, 4	22	330	7	+0.44	-0.06	5	+19
95...	12.34	11.80	+0.54	5, 5	25	306	54	+0.29	+0.25	17	+40
96...	13.84	13.59	+0.25	5, 4	22	341	10	+0.51	-0.26	7	+13
98...	12.86	12.60	+0.26	5, 5	25	321	37	+0.39	-0.13	15	+18
101...	14.03	13.64	+0.39	5, 4	22	312	7	+0.33	+0.06	5	+20
102...	13.96	13.33	+0.63	5, 4	22	366	10	+0.66	-0.03	7	+20
103...	14.49	13.75	+0.74	1, 1	5	379	3	+0.74	0.00	2	+23
104...	12.55	12.40	+0.15	5, 5	25	330	40	+0.44	-0.29	15	-6
107...	14.54	14.06	+0.48	5, 3	19	375	1	+0.72	-0.24	1	+20
108...	13.70	12.97	+0.73	5, 4	22	452	15	+1.19	-0.46	9	+24
114...	12.77	12.24	+0.53	1, 1	5	329	39	+0.43	+0.10	4	+24
115...	12.24	11.83	+0.41	5, 5	25	392	58	+0.82	-0.41	17	+46
116...	14.92	13.82	+1.10	5, 1	8	408	0	+0.91	+0.19	0	+44
117...	13.29	12.51	+0.78	5, 5	25	391	29	+0.81	-0.03	13	+32
118...	12.40	11.92	+0.48	5, 5	25	308	52	+0.30	+0.18	17	+53
121...	13.26	12.75	+0.51	5, 5	25	339	27	+0.49	+0.02	13	+29
124...	14.72	13.78	+0.94	5, 1	8	333	0	+0.45	+0.49	0	+32
127...	14.32	13.82	+0.50	5, 2	14	338	7	+0.48	+0.02	4	+42
131...	14.08	13.55	+0.53	5, 4	22	326	4	+0.41	+0.12	3	+6
134...	14.73	13.82	+0.91	5, 1	8	225	0	-0.22	+1.13	0	+11
135...	13.88	13.42	+0.46	5, 3	19	349	12	+0.55	-0.09	7	+26
136...	13.19	12.71	+0.48	5, 4	22	333	30	+0.45	+0.03	13	+32
138...	12.17	11.81	+0.36	5, 5	25	297	60	+0.24	+0.12	18	+41
139...	13.61	12.52	+1.09	5, 5	25	455	17	+1.20	-0.11	10	+11
141...	15.45	14.45	+1.00	5, 1	8	(+15)
143...	12.58	12.14	+0.44	3, 5	19	310	55	+0.31	+0.13	14	+66
145...	11.92	11.51	+0.41	5, 5	25	313	59	+0.34	+0.07	18	+41
147...	13.86	13.23	+0.63	5, 3	19	329	12	+0.43	+0.20	7	+42
148...	13.61	13.12	+0.49	5, 4	22	4325	17	+0.41	+0.08	10	+30

TABLE II—Continued

No.	MOUNT WILSON					HERTZSPRUNG			C_W minus $C_{H\lambda}$	WT. OF DIFF.	$P_{\lambda W}$ minus $P_{\lambda H\lambda}$
	P_β	P_γ	C_W	n	Wt. C	λ_e	Wt. λ	$C_{H\lambda}$			
153...	13.62	12.30	+1.32	5, 5	25	4507	16	+1.53	-0.21	10	+11
156...	14.66	13.68	+0.98	5, 1	8	463	1	+1.25	-0.27	1	+26
158...	14.52	13.72	+0.80	5, 1	8	338	3	+0.48	+0.32	2	+29
160...	14.63	13.66	+0.97	5, 2	14	321	0	+0.39	+0.58	0	+21
168...	14.49	13.78	+0.71	1, 1	5	360	0	+0.62	+0.09	0	+6
169...	13.32	12.95	+0.37	1, 1	5	342	24	+0.50	-0.13	4	+16
170...	13.93	13.33	+0.60	1, 1	5	4363	6	+0.64	-0.04	3	+10

Hence $\Delta C(MW) = +1.23$ mag. corresponds to $\Delta\lambda = 200$ Å and, finally, for

$$\Delta C(MW) = +1.00 \text{ mag.}, \Delta\lambda = 163 \text{ Å.}$$

The next step was the determination of λ_0 , the value of λ_e which corresponds to $C=0$. As the exact value of the grating constant was not available, λ_0 was obtained by combining the foregoing data as follows:

$$\lambda_0 = \frac{1.0780}{0.0558} \times 222 \text{ Å} - 0.21 \times 163 \text{ Å} = 4255 \text{ Å.}$$

There is here a computational uncertainty of ± 10 Å owing to the fact that the factor 222 Å is given only to the nearest angstrom, but probably this is within the uncertainty arising from other sources.

A rough control is afforded by Professor Hertzprung's classification of the spectra of the brighter stars photographed by Eberhard, which was also kindly placed at my disposal. From the 26 Å stars in this list the value $\lambda_0 = 4262$ was found on the assumption that the maximum frequency of occurrence is for stars of the type A0. From the same data Hertzprung finds for the median $\lambda_e = 4266$. The close agreement of these two values with that found above must not be accepted as an indication of a corresponding precision in the result, for presumably the value $\lambda_0 = 4234$ adopted by Hertzprung on the basis of all the material at his disposal is more reliable.

The difficulty in any comparison with spectra lies in the fact that the frequency distribution of the various types which applies to the stars in general does not necessarily hold for clusters. In

fact, for this particular cluster it appears that the maximum frequency is for stars approximately of type Fo, although there is a secondary, but much less conspicuous, maximum for the A stars. Then, too, there is a further difficulty with such a comparison in that we are not certain that the color-index of an Ao star belonging to the cluster is really zero.

In the absence of more definite information the value $\lambda_0 = 4260$ was adopted for the reduction, and the linear relation used for the transformation of the effective wave-lengths into color-indices was accordingly

$$163C_{Hz} = \lambda_e - 4260.$$

Had the value $\lambda_0 = 4234$ subsequently adopted by Hertzsprung been employed, the values of C_{Hz} would have been systematically larger by 0.16 mag. than those given in Table II.¹

IV. COMPARISON OF RESULTS

A comparison of the color results found by the two methods is shown by the differences $C_W - C_{Hz}$ in Table II. Although there are several large values among them, the corresponding weights usually are low. For a final comparison reference may be made

TABLE III
MEAN RESULTS FOR GROUPS OF STARS

MW Pg. Mag.		MW C.I.	REL. WT.	C_W minus C_{Hz}	REL. WT.	No STARS	Pg. Mag. MW minus C_{Hz}
Mean	Range						
12.1.....	11.69-12.34	+0.43	186	+0.02	132	8	+0.32
12.7.....	12.40-12.92	+0.35	149	-0.04	93	7	+0.26
13.3.....	13.03-13.49	+0.59	149	+0.04	83	7	+0.32
13.7.....	13.50-13.96	+0.78	253	-0.06	97	12	+0.24
14.3.....	14.03-14.49	+0.60	112	+0.10	20	7	+0.22
14.6.....	14.49-14.70	+0.91	119	+0.02	11	9	+0.23
14.9.....	14.72-15.45	+0.98	62	7	+0.30
Means...	13.7	+0.66	0.00	+0.27

to Table III which gives mean results for groups of stars. Here the agreement is very good, both in the progressive increase of the

¹In a recent letter Professor Hertzsprung writes that $\lambda_0 = 4234$ corresponds to a color-index whose value is zero with a mean error of the order of 0.05 mag.

color-index and in the absolute values; but it should not be overlooked that the latter are subject to a small constant error because of the uncertainty in the value of λ_0 .

The adopted system of weights requires a word of comment inasmuch as the two series $Wt._C$ and $Wt._A$ which appear in Table II originated quite independently of each other and are not necessarily directly comparable. An examination of the mean errors corresponding to unit weight showed, however, that they are very nearly on the same system; in calculating the weights of the differences $C_W - C_{Hz}$ it was therefore assumed that $Wt._C$ and $Wt._A$ are strictly homogeneous.

Of the 57 stars in Table II the value of $Wt._A$ is zero for 9 of the fainter objects; for one there is no value of λ_e , so that the results in Table III are based on 47 stars. Had the value $\lambda_0 = 4234$ been used, the mean difference $C_W - C_{Hz}$ for all the stars would have been -0.16 mag. instead of zero as shown in Table III. These results, 0.00 and -0.16 mag., respectively, indicate the uncertainty affecting the comparison, and, at the same time, the probable limits of the relative errors in the Mount Wilson photographic and photo-visual scales between the twelfth and the fifteenth magnitudes.

The only other scales extending into this region which have been connected with the international zero-point defined by the stars of the sixth magnitude are those of *H.C.*, No. 170. From the known relations which these bear to the Mount Wilson scales it is possible to compare at once the results from the effective wavelengths with those which would have been obtained had the Harvard magnitudes been used for the calculation of the color-indices.

For the region of the scale with which we are concerned we have

$$\begin{aligned} MW \text{ } Pg - HH &= +0.28 \text{ mag.} \\ MW \text{ } Pv - H \text{ } Vis &= 0.00 \end{aligned}$$

in which HH represents what has been called the Harvard homogeneous scale,¹ namely, the photographic scale of *H.C.*, No. 170,

¹ *Mt. Wilson Contr.*, No. 97; *Astrophysical Journal*, 41, 206, 1915. For the region in question $MW \text{ } Pg - H.C.$, No. 170 = $+0.40$ mag. The color correction to *H.C.*, No. 170, which reduces the results to a uniform system is $+0.04$ mag. Applying this and the zero-point correction of $+0.08$ mag. we have the foregoing value for $MW \text{ } Pg - HH$.

reduced to a uniform color system and corrected by $+0.08$ mag. to refer it to the international zero-point; the second relation is approximate and, strictly speaking, holds only for the twelfth magnitude. We therefore find

$$C_W - C_H = +0.28.$$

But from the preceding discussion

$$C_W - C_{Hz} = 0.00 \text{ or } -0.16$$

according to the value adopted for λ_0 .

These two equations cannot, however, be combined as they stand, for the values of C_{Hz} in the second relation refer to the Mount Wilson color system which differs from that of Harvard. The necessary modification is that corresponding to the substitution of 200 for 163 in the equation on p. 127. Since the mean color-index for the 47 stars is 0.66 mag., the values of C_{Hz} on the Harvard system will be 0.11 mag. less, on the average, than those found above. We therefore find

$$C_H - C_{Hz} = -0.17 \text{ or } -0.33 \text{ mag.}$$

which represents the mean difference in the color-indices derived from the effective wave-lengths and from the photographic and visual magnitudes of *H.C.*, No. 170.

In addition to the color results, Table III also shows a comparison of the Mount Wilson photographic magnitudes with those found by Hertzsprung. The scale for the latter was established with the aid of a grating used in connection with the Potsdam 80-cm refractor ("Halbgitter" method). The agreement is good, although there is a constant difference of $+0.27$ mag.; but this is of no significance, as Hertzsprung has determined the zero-point of his magnitudes by a comparison with Pleiades stars instead of with the Pole.

V. PROBABLE ERRORS

It is of interest, finally, to compare the two methods of determining the color of the stars from the standpoint of precision. The average deviation of a single magnitude as found above is ± 0.10 mag. The corresponding probable error for a color-index based

upon one photographic and one photo-visual magnitude is therefore ± 0.12 mag., while that for the mean of five such determinations is ± 0.054 mag. This indicates sufficiently the precision with which relative values of the color have been determined. In estimating the uncertainty of the absolute values of the color-indices, allowance must also be made for the zero-point errors. In this case their effect upon the color-index is of the order of ± 0.04 mag.

Hertzsprung gives as the mean error of a single effective wave-length 26 Å, which corresponds to a probable error of about ± 0.11 mag. For absolute determinations a zero-point error has also to be considered. This includes, first, the uncertainty in the adopted value of λ_0 which is used for the reduction of all the plates, and, second, a systematic plate error which seems to be of the order of 10 Å.¹ The data relating to the error in λ_0 are not available; but since this is an instrumental constant whose value is determined once for all, its error can be made negligible by an appropriate investigation. In the matter of precision, therefore, there seems to be little choice between the two methods.

SUMMARY

Star colors may be determined by measuring the mean effective wave-length of the light of individual stars or by deriving their color-indices. Since the latter depend directly upon the photographic and the visual, or photo-visual, magnitudes, a comparison of color results found by the two methods affords a control upon the relative errors of the magnitude-scales; the fainter the stars the more important is the control.

Such a comparison has been made for 47 stars in N.G.C. 1647. The effective wave-lengths used were those by Hertzsprung. The color-indices were found by transferring the Mount Wilson photographic and photo-visual scales for stars near the Pole to the region of the cluster. The mean of the differences between the color-indices calculated from the effective wave-lengths and those derived from the magnitudes is

$$C_W - C_H = 0.00 \text{ or } -0.16 \text{ mag.}$$

¹ *Mt. Wilson Contr.*, No. 100; *Astrophysical Journal*, 42, 92, 1915.

according as 4260 Å or 4234 Å is adopted as the effective wavelength of a star whose color-index is zero.

The comparison includes stars between photographic magnitudes 11.5 and 15. Within this interval the two series of color-indices show the same increase in the mean color with increasing magnitude. The relative errors of the magnitude-scales seem to be within the uncertainty affecting the reductions of the effective wave-lengths.

MOUNT WILSON SOLAR OBSERVATORY

March 4, 1915